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Interfacial degradation mechanisms with applications to polymer-matrix composites and intergranular stress corrosion cracking of steels

Denizhan Yavas
Iowa State University

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Interfacial degradation mechanisms with applications to polymer-matrix composites and intergranular stress corrosion cracking of steels

by

Denizhan Yavas

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Engineering Mechanics

Program of Study Committee:
Ashraf F. Bastawros, Major Professor
Kurt R. Hebert
Wei Hong
Stephen Holland
Pranav Shrotriya

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2018

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DEDICATION

This dissertation is dedicated to my parents, Cavide and Osman, who have always loved me unconditionally and taught me to work hard for the things that I aspire to achieve. They have been a constant and everlasting source of encouragement during my entire life. Additionally, they have always managed to motivate and help me to find hope even in the darkest days. I am truly thankful for their understanding, patience, love and support.
TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... vi
LIST OF TABLES ............................................................................................................. xiv
NOMENCLATURE ........................................................................................................... xv
ACKNOWLEDGMENTS ................................................................................................... xvi
ABSTRACT ..................................................................................................................... xviii

CHAPTER 1. OVERVIEW ................................................................................................. 1
   Introduction: Interfacial Fracture of Adhesively Bonded Composite Structures .......... 1
   Adhesively Bonded Composite Structures ................................................................. 1
   Structural Reliability of Adhesive Joints .................................................................... 3
   Failure of Adhesively Bonded Composites ............................................................... 8
      Failure Modes ......................................................................................................... 8
      Interfacial Fracture Mechanics ............................................................................. 10
      Experimental Methods ......................................................................................... 12
      Numerical Methods .............................................................................................. 14
   Introduction: Intergranular Stress Corrosion Cracking ............................................ 16
   Thesis Organization ................................................................................................. 21
   References .................................................................................................................. 25

CHAPTER 2. UTILIZATION OF NANOINDENTATION TO EXAMINE BOND LINE INTEGRITY IN ADHESIVELY BONDED COMPOSITE STRUCTURES .......... 32
   Abstract ..................................................................................................................... 32
   Introduction ............................................................................................................... 33
   Proposed Hypothesis ............................................................................................... 35
   Material and Sample Preparation ............................................................................. 39
      Adhesive Material and Contaminant Types .......................................................... 39
      Sample Preparation .............................................................................................. 40
   Hardness Measurements by Nanoindentation ......................................................... 42
   Mode-I Fracture Toughness Measurements by Double Cantilever Beam Test ........ 44
   Numerical Modeling ................................................................................................. 49
      Computational Model ......................................................................................... 49
      Comparison with Experiment ............................................................................. 52
   Numerically Augmented Experimentally Derived Scaling ....................................... 55
   Conclusion .................................................................................................................. 59
   References .................................................................................................................. 60
CHAPTER 3. MODE-I FRACTURE TOUGHNESS AND SURFACE MORPHOLOGY EVOLUTION FOR CONTAMINATED ADHESIVELY BONDED COMPOSITE STRUCTURES ................................................................. 63
  Abstract........................................................................................................... 63
  Introduction ..................................................................................................... 64
  Material and Sample Preparation .................................................................. 67
  Experimental Procedure ................................................................................ 69
  Numerical Modeling Approach .................................................................... 70
  Experimental Results .................................................................................... 73
    Effective Bond Line Fracture Toughness .................................................. 73
    Role of Contamination on Interfacial Crack Growth and Morphology ...... 78
  Numerical Results and Discussions ............................................................ 81
    Calibration of Cohesive Zone Parameters ............................................... 81
    Contamination-induced Limitation of Plastic Energy Dissipation in Bond Line ..... 83
  Conclusion ................................................................................................... 87
  References .................................................................................................... 88

CHAPTER 4. PREDICTION OF INTERFACIAL SURFACE ENERGY AND EFFECTIVE FRACTURE ENERGY FROM CONTAMINANT CONCENTRATION IN POLYMER-BASED INTERFACES ................................................. 92
  Abstract........................................................................................................... 92
  Introduction ..................................................................................................... 93
  Experimental and Modeling Framework ..................................................... 94
  Results ........................................................................................................... 96
  Predictive Correlation Laws ....................................................................... 101
  Summary ....................................................................................................... 105
  References .................................................................................................... 106

CHAPTER 5. CORRELATING INTERFACIAL FRACTURE TOUGHNESS TO SURFACE ROUGHNESS IN POLYMER-BASED INTERFACES .............................................................. 109
  Abstract........................................................................................................... 109
  Introduction ..................................................................................................... 110
  Method and Results ...................................................................................... 113
  Discussion...................................................................................................... 120
  Conclusion ..................................................................................................... 124
  References .................................................................................................... 124

CHAPTER 6. MORPHOLOGY AND STRESS EVOLUTION DURING THE INITIAL STAGES OF INTERGRANULAR CORROSION OF X70 STEEL ................................................................. 127
  Abstract........................................................................................................... 127
  Introduction ..................................................................................................... 128
  Experimental Details ..................................................................................... 130
  Results and Discussion ................................................................................ 132
    Electrochemical Measurements ............................................................... 132
    Large-angle Cross-section Samples ......................................................... 134
    Small-angle Cross-section Samples ......................................................... 137
    Transient Electrochemical and Stress Measurements .............................. 145
## LIST OF FIGURES

| Figure 1-1 | Comparison between a riveted and an adhesively bonded joints in terms of the effective non-reinforced span (left column) and the stress distribution over the joint (right column) (adopted from Ref. [2]). | 2 |
| Figure 1-2 | Schematic model for explaining the role of bond line thickness on the maximum volume of plastic deformation, and thereby resulting effective bond line toughness. The dashed regions show plastic process zones in front of the crack tips. (adopted from Ref. [28]) | 5 |
| Figure 1-3 | An illustration of various types of defects (adopted from Ref [2]). | 6 |
| Figure 1-4 | The variation of mode-I bond line toughness for different sources of degradation, along with the ultrasonic inspection intensity maps for the three cases (adopted from Ref. [10]). | 7 |
| Figure 1-5 | Sketches representing failure modes on adhesively bonded CFRP-joints (adopted from Ref. [34]). | 9 |
| Figure 1-6 | The fracture surfaces of double cantilever beam fracture test samples, prepared by using different surface pre-treatment procedures, which leads to different types of failures: (a) adhesive, (b) cohesive, and (c) mixed-type failure. | 10 |
| Figure 1-7 | (a) Cohesive traction-separation law for the adhesive layer. (b) Sketch of the line bond separation, showing the different cohesive separation stages: (A) start of adhesive yielding, (B) interfacial debonding (damage initiation), and (C) full separation (fully damaged). | 12 |
| Figure 1-8 | (a) Tensile samples for bulk properties. (b) DCB sample and testing procedure. | 13 |
| Figure 1-9 | The bilinear traction-separation curve. | 15 |
| Figure 1-10 | Material cross-sections of high strength steels, showing (a) intergranular SCC under high-pH conditions, (b) transgranular SCC under nearly neutral-pH conditions. (both images are magnified 250 times). (adopted from Ref. [69]). | 17 |
| Figure 1-11 | Schematic current-potential curve showing range of maximum susceptibility to SCC for a steel in carbonate/bicarbonate solution (Adopted from Ref. [70]). | 18 |
Figure 1-12 Schematic diagram of a typical SCC evolution, logarithm of crack growth rate as a function of the crack tip stress intensity factor, showing three regimes of crack propagation with different rates. .................................................. 19

Figure 1-13 (a) A composite transmission electron microscopy (TEM) image, showing the dislocation pile-up density near by a grain boundary with hydrogen atoms (lighter lines) and without hydrogen atoms (darker lines) in the material (Adopted from Ref. [74]). (b) Scanning electron microscopy images of fracture surface of hydrogen pre-charged single edge notch fracture X65 steel sample, highlighting surface micro/nano dimples associated with hydrogen-induced nano-void coalescence mechanisms (adopted from Ref. [77]). .................................................................................................. 20

Figure 2-1 (a) Summary of TH numerical results (Fig 8, Ref. [11]), showing the correlation between the ratio of the effective work of fracture per unit area to the interfacial work of separation, and the ratio of interfacial cohesive strength to the yield strength of the adhesive layer for two different hardening exponent. (b) Geometry of the bond line joint. .................................................. 38

Figure 2-2 Double cantilever beam specimen geometry.................................................. 41

Figure 2-3 Role of different contaminants on the measured indentation modulus. Error bars correspond to ±STDEV ............................................................ 43

Figure 2-4 Role of different contaminants on the measured indentation hardness. Error bars correspond to ±STDEV. ............................................................ 44

Figure 2-5 (a) Force-displacement curves and (b) derived fracture energy release rate curves, obtained from DCB experiments, along with the numerical results (dashed lines) for the examined cases. .................................................. 45

Figure 2-6 Summary of effective fracture toughness measurements for the examined cases at the same level of contamination concentration (55 µg/cm²), highlighting the severe chemical degradation of the adhesive strength, inserts show optical images of the fracture surfaces of the reference (uncontaminated) and HF-1 contaminated cases.................................................. 47

Figure 2-7 Correlation between experimentally measured effective bond line fracture toughness and bond line indentation hardness. All results are normalized by those of HF-1 contaminated case. ............................................................ 48

Figure 2-8 The utilized bilinear traction-separation law, showing self-similar scaling approach to model degradation. ............................................................ 50
Summary of the numerical results for $\Gamma_{\text{eff}}$ with sets of $\Gamma_0$ and $\hat{\sigma}$, mapping the experimental cases.

Summary of numerical study showing the interplay between the cohesive parameters and the bond line yield strength on the effective fracture toughness. The experimental data (filled symbols) transcends across multiple groups of interface properties. All results are normalized by those of HF-1 contaminated case.

Correlation between the ratio of effective fracture toughness to calibrated interfacial cohesive toughness and the ratio of interfacial cohesive strength to yield strength for $\Gamma_{\text{eff}}$ and $\sigma_y$ measured experimentally, while $\Gamma_0$ and $\hat{\sigma}$ calibrated numerically on logarithmic scale.

Correlation between the numerically calibrated interfacial cohesive toughness and the experimentally measured hardness. All results are normalized by those of HF-1 contaminated case.

(a) Experimental loading configuration for the double cantilever beam test (b) Typical force-displacement curve, showing the initial loading-unloading step to sharpen the manufactured blunt notch, followed by the reloading step with a steady state interfacial crack propagation.

(a) Finite element model geometry, mesh and boundary conditions. (b) The utilized bilinear traction-separation law, showing self-similar scaling approach to model degradation.

Summary of the experimental results for the examined cases, showing the DCB force-displacement curves and the derived fracture energy release rate, G.

(a) Summary of effective fracture toughness measurements for the examined cases as a function of contamination concentration, highlighting the severe chemical degradation of the bond line toughness. (b) The observed correlation between the normalized effective fracture toughness and the contaminant concentration.

The measured force and crack length as a function of the applied displacement, showing the distinct changes in the failure modes. (a) Control case showing ductile fiber-tear type failure. (b) contaminated case showing brittle adhesive-type failure.

Optical and SEM images of the fracture surfaces. (a, b) Control case exhibiting rough fracture surface with hackle marks, associated with fiber-
tear-type failure mode. (c, d) Level J contamination case showing a thin adhesive layer covering the fibers, consistent with adhesive-type failure mode.

Figure 3-7 (a) A representative set of force-displacement curves and (b) the corresponding fracture energy release rate G-curves, obtained from DCB experiments, along with the numerical results (dashed lines), for the examined cases.

Figure 3-8 The experimentally measured and numerically calibrated variation of the effective interface toughness $G_{eff}$ (circles) and the intrinsic fracture toughness $G_0$ (squares) as a function of the cohesive strength $\hat{\sigma}$, highlighting the role of the contamination level.

Figure 3-9 The opening stress ($\sigma_{22}$) contours in the vicinity of interfacial crack for the control and level J contamination cases, highlighting the constraint effect of level J contamination on the extent of plastic process zone size in front of the interfacial crack tip within the adhesive layer.

Figure 3-10 Summary of the numerical estimates of bond line process zone size as a function of cohesive strength to yield strength ratio. The insert depicts the effective plastic strain contours within the adhesive layer showing the wake of plasticity behind the interfacial crack for the control and level C contaminated cases, highlighting the limited plastic dissipation with level C contamination.

Figure 4-1 (a) A representative set of force-displacement curves and (b) the corresponding fracture energy release rate G-curves, obtained from DCB experiments, along with the numerical results (dashed lines), for the examined cases.

Figure 4-2 Optical images of the fracture surfaces of (a) the control, (b) 3 $\mu$g/cm$^2$, and (c) 55 $\mu$g/cm$^2$ contaminated cases, showing the marked difference in roughness.

Figure 4-3 Topologies of the fracture surface, measured by 3D non-contact surface profilometer with 1.45x1.05 mm$^2$ field of view. (a, b) 3D rendering of the fracture surface topologies. (c, d) Height profiles along the marked lines, showing the roughening and extent of plasticity in the control case, and the smooth profile in the 55 $\mu$g/cm$^2$ contaminated case.

Figure 4-4 Summary of the experimentally measured macroscopic fracture energy (solid squares) and the numerically calibrated interfacial surface energy (open squares) as a function of contamination concentration. The error bars
The dashed and dotted lines stand for the corresponding predictive correlations of Eqs. (3) and (6).

Figure 5-1 Summary of effective fracture toughness measurements as a function of contaminant concentration in log-scale, highlighting the severe chemical degradation of the interfacial toughness. The reference fracture toughness level for the uncontaminated bond line is presented by the shaded area, with \( \pm \text{STDEV} \) interval. The insert shows a scanning electron microscope image of the adhesive material, revealing the aluminum powder particles size embedded in the adhesive.

Figure 5-2 The change in fracture surface RMS roughness measured over 1.45x1.45 mm\(^2\) area for varying effective fracture toughness. The insert optical images show the crack propagation profile and the corresponding fracture surface for two different interfacial toughness level, revealing the variation of smoothness of the fracture surface with the interfacial roughness.

Figure 5-3 Scanning electron microscope images of fracture surfaces for (a) the reference case, revealing a roughened fracture surface with hackle marks on the fibers, and (b) the most severe (55\(\mu\)g/cm\(^2\)) contamination case, showing a smoother fracture surface with a thin layer of residual adhesive on the fibers. The dashed arrows indicate the crack propagation direction.

Figure 5-4 3D rendering of the fracture surface topologies along with the typical height profiles along crack propagation direction (sampled along \( y=0.25\text{mm} \) line) for the three different level of the toughness. The arrows represents the crack growth direction.

Figure 5-5 (a) A representative set of height-height correlation functions along the crack propagation direction for the three different level of toughness, showing the self-affine nature within the smaller length scales with the roughness exponent \( \beta = 0.35 \pm 0.02 \) independent of the toughness value, and the upper bound of the self-affinity defined as the cut-off length scale \( \xi \), (b) the correlation between the cut-off length scale and the measured effective bond line toughness for the examined cases.

Figure 5-6 (a) The variation of the estimated length scale for the process zone size (\( R_0 \)) with the measured interfacial toughness, (b) the predicted correlation between \( R_0 \) and \( \xi \).

Figure 6-1 Electrochemical measurements during corrosion of X70 steel in 1 M NaHCO\(_3\). (a) Linear sweep voltammetry showing the three test potentials.
used in other experiments. (b) Current density transients for the experiments used for morphology observations in Figs. 4-7. .......................... 133

Figure 6-2 Large-angle cross section views after corrosion at -0.521 V. (a) 2 hr exposure; sample prepared by FIB etching, cross section plane 52° from horizontal. (b) 4 hr exposure; sample prepared by polishing, cross section plan 90° from horizontal. Dashed lines indicate triangular wedge features produced by corrosion at the alloy-corrosion product interface. The angles of the wedge apex are marked in the image. ............................................ 135

Figure 6-3 Height profile measured by optical profilometry after 2 hr exposure at -0.521 V and followed by removal of corrosion product. Curve to the left of the arrow represents an area that was not exposed to solution......................... 136

Figure 6-4 Small-angle cross section views of X70 steel after 2 hr corrosion at -0.521 V. Sample was prepared by shallow-angle polishing. Panels (b) - (e) are high-magnification images at the points indicated in the low-magnification image (a). .......................................................... 139

Figure 6-5 Schematic depiction of triangular wedge morphology of intergranular corrosion. .................................................................................................. 140

Figure 6-6 Composition of grain boundary corrosion product film on sample exposed for 2 hr at -0.521 V. (a) SEM showing location of EDS line scan. (b) Composition profile along the line scan. .......................................................... 141

Figure 6-7 Small-angle cross section views of X70 steel after 2 hr corrosion at -0.478 V. Sample was prepared by shallow-angle polishing. Panels (b) and (c) are high-magnification images at the points indicated in the low-magnification image (a). .......................................................... 143

Figure 6-8 Small-angle cross section views of X70 steel after 2 hr corrosion at -0.575 V. Sample was prepared by shallow-angle polishing. Panels (b) and (c) are high-magnification images at the points indicated in the low-magnification image (a). .......................................................... 144

Figure 6-9 Stress and current density measurements during corrosion exposures at the three test potentials. (a) Force per width (solid lines) and current density (dashed lines) transients. (b) Charge density transients obtained by integrating the current density in (a). ............................................ 146

Figure 7-1 (a) Anodic current density transient at -0.521 V. (b-d) SEM images of shallow angle polished section of steel sample after 2h corrosion at -0.521 V. .................................................................................................. 159
Figure 7-2  (a) AFM image in surface gradient mode showing the grain boundary and the locations of the imposed lines of nanoimprints. (b) A representative set of force-indentation depth curves for the indents on line 3 at distances 0.25 µm (blue) and 1.75 µm (green) from the GB within grain 1. The dashed line shows the Hertzian fit for spherical indenter tip. ............................................... 161

Figure 7-3  Variation of hardness $H$ and modulus $E$ across the GB for the indentation lines 1, 2 (a), line 3 (b), and line 4 (c) in Figure 7-2. CP designates corrosion product................................................................. 163

Figure 8-1  (a) SEM image of the polished surface, showing the IGC attach at the triple junctions, (b) AFM image in surface gradient mode showing the grain boundary and the locations of the imposed lines of nanoimprints, (c) A representative set of force-indentation depth curves for the indents on line 2 at different distances from the GB, along with Hertzian fit for spherical contact. (d) The summary of critical load for the first displacement burst (normalized by the critical loads obtained for the interior of the grains), presented as a function of distance from GB................................................................. 172

Figure 8-2  (a) MD simulation box, showing the iron atoms (blue), and the atoms surrounding the lattice vacancies. (b) load-indentation depth curves for different vacancy concentration, (c) load-indentation depth curves for different hydrogen atom concentration. (d) The summary of the critical load for the dislocation nucleation (normalized by the that of the perfect crystal) as a function of the concentration, along with the experimental results................................................................. 177

Figure 8-3  (a-c) Snapshots of the atomistic configuration showing the dislocation nucleation and mobility for the perfect crystal, highlighting the dislocation nucleation taking place right underneath the indenter tip. (d-f) the corresponding von misses stress field underneath the indenter tip on (1 0 0) plane. ........................................................................................................ 179

Figure 8-4  (a-c) Snapshots of the atomistic configuration showing the dislocation nucleation and mobility for the 0.1% vacancy case, highlighting the nucleation of the dislocation loop near by a vacancy cluster. (d-f) the corresponding von misses stress field underneath the indenter tip on (1 1 0) plane. ........................................................................................................ 180

Figure 9-1  (a) The pipeline wall, from which samples were machined, (b-c) scanning electron microscope images showing the microstructure on the longitudinal-short transverse panel. The dark gray-shaded areas represent the ferrite phase, while the light gray-shaded elongated regions show the pearlite phase. ................................................................. 191
Figure 9-2  (a) the anodic dissolution current density transients at this potential for two different exposure times, (b, c) scanning electron microscope images showing the corroded surface after the 15 min and 2h corrosion exposure, respectively ................................................................. 193

Figure 9-3  (a) Scanning electron microscope image (SEM) of the angle-polished surface of 2h corrosion sample, revealing three distinct layers, and higher magnification SEM images of the top corrosion product layer (b, c), and IGC –affected layer (d, e) .................................................................................. 194

Figure 9-4  (a) Higher magnification scanning electron microscope image (SEM) of a triple junction in the IGC affected layer. (b-d) Fe, O, and Si content intensity maps, respectively. (e) EDS spectra of the selected region. ........... 195

Figure 9-5  3D surface profiles measured by non-contact optical profilometer for (a) 2h and (b) 1h corrosion samples, showing the corrosion product layer at edges of exposure regions, with a field of view of 550 x 550μm². ......................... 197

Figure 9-6  The height profiles along the lines A, B, and C marked on (a, b) ............... 198

Figure 9-7  (a) A representative set of indentation load-depth curves for the base (no corrosion), 1h and 2h corrosion samples corroded samples, (b) Indentation modulus as a function of penetration depth for the examined cases. ........... 200

Figure 9-8  The variation of the continuously measured indentation (a) modulus and (b) hardness as a function of penetration depth for the examined layers. The inserts depict atomic force microscopy surface scans of a group of indent imprints in the IGC and CP layers ............................................................................. 203

Figure 9-9  The square of the measured hardness as a function of reciprocal of the penetration depth for the selected data sets, along with the NG model linear fitting curves for the different material constants ........................................... 206

Figure 9-10  SEM images of the surface of the 2h corrosion sample after removal of the top corrosion product layer by the diluted acetic acid solution, highlighting nano-dimples or cluster of nano-dimples, which can be perceived as traces of the high concentration vacancies cluster on the wall of GB grooves ........ 209
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>Different classes of contaminants used in this study.</td>
<td>40</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Calibrated CZ parameters and measured yield strength for the reference and all contamination cases.</td>
<td>52</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>The numerically calibrated interfacial fracture parameters for the examined contamination concentrations. (* Average values with standard deviation).</td>
<td>82</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>The numerically calibrated interfacial fracture parameters for the examined cases (* Average values presented with the corresponding standard deviation).</td>
<td>95</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
<td></td>
</tr>
<tr>
<td>CFRP</td>
<td>Carbon Fiber Reinforced Polymers</td>
<td></td>
</tr>
<tr>
<td>CZM</td>
<td>Cohesive Zone Method</td>
<td></td>
</tr>
<tr>
<td>DCB</td>
<td>Double Cantilever Beam</td>
<td></td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>ENF</td>
<td>End Notched Flexure</td>
<td></td>
</tr>
<tr>
<td>ELS</td>
<td>End Loaded Split</td>
<td></td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Method</td>
<td></td>
</tr>
<tr>
<td>GB</td>
<td>Grain Boundary</td>
<td></td>
</tr>
<tr>
<td>IGC</td>
<td>Intergranular Corrosion</td>
<td></td>
</tr>
<tr>
<td>IGSCC</td>
<td>Intergranular Stress Corrosion Cracking</td>
<td></td>
</tr>
<tr>
<td>IR</td>
<td>Infra-Red</td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
<td></td>
</tr>
<tr>
<td>MMB</td>
<td>Mixed Mode Bending</td>
<td></td>
</tr>
<tr>
<td>NDE</td>
<td>Non-destructive Evaluation</td>
<td></td>
</tr>
<tr>
<td>SCC</td>
<td>Stress Corrosion Cracking</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
<td></td>
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<td></td>
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<tr>
<td>3D</td>
<td>Three-dimensional</td>
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</tbody>
</table>
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ABSTRACT

Structural interface property controls a wide spectrum of applications, ranging from the hybrid integration of dissimilar structural materials, to the enhanced physical properties of high performance engineering alloys. Practically, interfaces can be perceived as the weakest part of a heterogeneous material or a structure. They are the most prone to environmental disturbances such as chemical or thermal, with significant deterioration of the structural integrity. Despite the large volume of literature on the topic, there remains a lack of proper understanding of degradation mechanisms of these interfaces. The challenge remains in the early detection of interfacial damage, and assessment of the remaining safe service life. This work is an attempt to provide some physical and mechanical understanding of these interfacial degradation mechanisms in two problem sets; (1) contamination-induced interfacial degradation in polymer matrix composites, and (2) early stage degradation of microstructure and mechanical properties in pipeline steels. The ultimate goal is to provide metrics for the physical and mechanical changes associated with these degradation mechanisms, and provide the bases for further development of new nondestructive evaluation techniques.

For the first topic, the contamination-induced degradation mechanisms in polymer-matrix interfaces were examined experimentally and the observed trends were rationalized analytically and numerically. Two complementary frameworks were developed for the prediction of residual interfacial fracture energy, based on the changes in the adhesive hardness, and the level of the surface contaminants. Both of these quantities can be measured nondestructively by nanoindentation and IR-spectroscopy, respectively. Additionally, role of bond line contamination on mode-I failure and fracture surface evolution is quantified by
performing statistical fracture surface analysis. With additional examination of other material systems, the proposed correlations may provide the basis for nondestructive evaluation of bond line integrity.

For the second topic, initial microstructure surface evolution was examined in high strength steel under corrosive environment. The environmentally occurring corrosion process is mimicked by laboratory scale electrochemical experiments. Nanoindentation technique was utilized to locally characterize the mechanical property degradation in the sub-surface layer of a pipeline steel undergoing intergranular corrosion at active dissolution potentials at pH 8.2. Additionally, atomistic computational analysis was conducted to rationalize the experimentally observed trends. The present study reports two key observations: (1) mechanically degraded grains in the subsurface layer with 10% reduction in hardness, (2) 1 μm-thick mechanically degraded layers adjacent to corroded grain boundaries with 25% lower hardness relative to the grain interior. The observed degradation is attributed to weakening of lattice resistance arising from the clusters of non-equilibrium atomic vacancies generated by the preferential dissolution of silicon atoms by intergranular corrosion activity. The findings might provide a new insight for the corrosion process and might suggest a mitigation strategy.
CHAPTER 1. OVERVIEW

Introduction: Interfacial Fracture of Adhesively Bonded Composite Structures

Adhesively Bonded Composite Structures

Adhesives have been an essential part of tool-making and used in many different forms for thousands of years in the history of humanity. The earliest form of adhesive-like substances in the human history is believed to be “tar”, which is a dark black viscous liquid of hydrocarbons and can be produced from natural organic materials such as coal and wood. An archaeological study showed that it was used to bond two stone flakes to each other in order to produce a primitive axe in the Middle Pleistocene era (circa 200,000 years ago) [1]. In the early ages, the adhesives were obtained from all different types of natural substances such as plants, milk, and skin. Since 1990s, polymer-based adhesives have been widely used in a diversity range of applications.

Adhesively bonded carbon fiber reinforced polymer (CFRP) composite joints have been extensively utilized in the aerospace industry, with the advantage of a high strength-to-weight ratio [2-4]. They are very promising alternatives to traditional mechanical joints such as rivets and fasteners, commonly used in metal-metal bonding applications. The application of traditional mechanical joining techniques to composite materials results in fiber cuts accompanied with stress concentrations and reduced structural integrity [2]. The introduction of adhesive joining has resolved many of these issues, with the advantages of relatively more uniform stress transfer along the bond line and high structural stiffness by reducing the
effective non-reinforces span length as shown in Fig. 1-1. They also provide excellent design flexibility for assembly of complex CFRP airborne structures [2].

Figure 1-1 Comparison between a riveted and an adhesively bonded joints in terms of the effective non-reinforced span (left column) and the stress distribution over the joint (right column) (adopted from Ref. [2]).

However, adhesive joints have not been efficiently used due to the lack of comprehensive material models with fatigue-like or damage evolution failure criterion [3]. As a result, adhesive joints are over-designed with the inclusion of mechanical fasteners as additional safety precautions. Additionally, environmental exposures have a detrimental effect on the mechanical performance and long-term reliability of the entire bonded structure [2]. In practice, exposure to environmental contamination represents one of the major technical challenges for subsequent composite repair, with stringent requirements for surface preparation and cleaning [5, 6].
Structural Reliability of Adhesive Joints

The structural reliability of adhesively bonded joints has been broadly studied under a wide range of environmental exposures, including service temperature [7-12], moisture [10-14], chemical contaminants [10, 15-17], and radiation [18]. In addition, the effect of harsh environmental conditions such as hydrothermal or chemical on the mechanical and physical properties of polymer-based adhesives was extensively studied [19-23]. The degradation process typically occurs through hydrolysis, oxidation, and dehydration reactions in the polymer chain [20]. The hydrothermal ageing of glass (or carbon) fiber/epoxy was shown to follow Fickian diffusion mechanism till saturation of the adhesive interface [21, 22]. Similarly, supported by atomistic simulations and experimental analysis, the diffusion coefficient of the water in a thermoset polymer decreased with increasing epoxy density [23]. The reduction in the elastic modulus of the epoxy was attributed to the water-induced swelling, while the reduction of strain to fracture was attributed to water-ingression [23].

The observed interfacial degradation mechanisms under different exposures were found to be very sensitive to the examined adhesive/adherend material systems. For example, it was shown that the rubber-steel peel strength can be degraded by 50% with a trace level (less than 1µg/cm²) of plasticizer contaminant, whereas, it can be improved due to exposure to hydraulic oil [24]. Additionally, the adhesive bulk property degradation was very different when utilized in a bonded joint. For example, the strength of the bulk adhesive material has shown a modest reduction (~10%) with high levels of calcium grease contamination [25]. Whereas, the same adhesive material has shown a significant interfacial deterioration at a low level of the same contamination [25]. Such observations highlight the complex interaction of the contamination on the mechanical properties of the adhesively bonded joints. It would
affect the confined local plastic deformation of the adhesive, while concurrently greatly deteriorating the intrinsic interfacial adhesion of the adhesive-adherend pair.

Such dual interaction between the intrinsic interfacial adhesion and the local dissipation within the adhesive would affect the effective macroscopic bond line toughness. For example, increasing the testing temperature would drastically decrease the mode-I fracture toughness of the bond line [8]. This trend was attributed to adhesive strength reduction above the glass transition temperature, despite the increase in its ductility. Similarly, preexisting moisture in the CFRP composite substrates would lead to a reduction in glass transition temperature of the adhesive after the bonding process, accompanied by significant degradation in the bond line fracture toughness [13].

Aside from the service environment, it was also established in layered structure literature that limiting the role of plastic dissipation within the adhesive layer by reducing its thickness would have a marked effect on the macroscopically measured fracture toughness of the bond line [25-28]. Figure 1-2 schematically depicts the correlation between the bond line thickness and the effective bond line toughness. Such correlation is imposed by the constraint effect of the bond line thickness on the volume of the plastic deformation within the adhesive layer. The maximum effective bond line toughness can be obtained for a particular bond line thickness, which maintains less restrictive effect on the development of the plastic process zone. However, the macroscopic bond line toughness tends to decrease for relatively smaller or larger bond line thicknesses due to restriction of the further development or the decrease in degree of contrasting reducing the length of the plastic process zone, respectively. It should also be noted that the shape of such correlation curve is highly dependent on the bond line width.
Figure 1-2  Schematic model for explaining the role of bond line thickness on the maximum volume of plastic deformation, and thereby resulting effective bond line toughness. The dashed regions show plastic process zones in front of the crack tips. (adopted from Ref. [28])

Another critical aspect related to adhesively bonded joints is the accurate assessment of the residual bond line strength and safe-life. A various types of non-destructive evaluation techniques (ultrasonic techniques, acoustic emission techniques, holographic techniques, thermography, radiographic techniques) have been utilized to predict the residual strength [29]. However, the direct measurement of the residual bond line strength or toughness is not non-destructively possible. Therefore, NDE techniques can only provide a correlation between the physically measured property such as bond area or interfacial stiffness and the projected bond line strength. The predicted bond line toughness might not always reliable due to the complex physical and chemical interplay between different degradation sources. Figure 1-3 depicts an illustration showing values types of defects, which might possibly exist in a bond line. For example, in one scenario, measuring bond line stiffness may not
necessarily give a good correlation with the residual strength in case of existence of micro-crack in the adhesive layer.

![Image](image.png)

**Figure 1-3** An illustration of various types of defects (adopted from Ref [2]).

In another scenario, measuring the void content of bonding area by ultrasonic inspection might not give the best prediction every time. Figure 3-4 presents an obvious example for such argument, showing variation of mode-I bond line toughness under different sources of degradation, along with the ultrasonic inspection of the three cases. In the ultrasound scan images, the light gray-shaded regions indicate good bonding quality (low porosity), whereas the dark gray-shaded regions represent bad bonding quality (relatively higher porosity). Interestingly, the thermal degradation resulted in a significant reduction in the bond line toughness, even though the ultrasonic inspections predict a bond line quality as good as that of the reference bond line. However, the bond line exposed to moisture can still provide 80% of the base line toughness, although the ultrasonic scans exhibit significantly high porosity compared to the reference bond line. Therefore, the challenge remains in the early detection of the interfacial progressive damage of the bonded structures and the
assessment of the current level of the effective interfacial fracture toughness, before the onset of a catastrophic failure.

Figure 1-4  The variation of mode-I bond line toughness for different sources of degradation, along with the ultrasonic inspection intensity maps for the three cases (adopted from Ref. [10]).

In addition, the interface topology and geometric roughness have a key role in changing the bond line quality. A large number of surface treatment processes are being used to modify the adherend surfaces prior to the bonding. They can be collected into three main groups: (1) mechanical, (2) chemical and (3) electrochemical surface treatments [2]. A combination of any of these groups such as chemical-mechanical treatment can also be applied. First, mechanical treatments typically target to remove (e.g. native oxide layers in metallic applications) and/or introduce macro-scale surface roughness on the adherend.
surface. The interlocking mechanism through the penetration of adhesive into the micro-asperities created by the mechanical surface treatment has a significant effect on the bond line strength [30]. Moreover, microscale roughness facilitates uniform distribution of the applied stress over the bond line, instead of concentration at the surface, and thereby enhances level of plastic energy dissipation within the bond line [31]. Second, chemical treatments can generally be considered as an etching process, which is used to reduce organic or inorganic surface layer, and/or produce chemical conversion coatings [2]. Etch solutions are commonly composed of sole or mixed strong acids for most of the metal applications. A various level of surface roughness can be crafted by chemical surface treatment, which enables an excellent control on the resulting bond quality [32]. Third, electrochemical surface treatments are generally considered as very costly and time consuming processes and only utilized for metal applications where precise control on the adherend surface is required. In particular, anodizing is one of the commonly used processes, especially for aluminum and titanium and their alloys. For example, in anodization of aluminum surface, formation of very thin porous anodic oxide film (mostly in hexagonal closed pack structure) can provide outstanding adhesion [2]. Overall, the surface pre-treatment processes aim to alter the interface properties such as wettability, geometric roughness, mechanical and electrochemical stability, and hence the bond line quality [33].

**Failure of Adhesively Bonded Composites**

**Failure Modes**

Failure modes of adhesively bonded joints can be classified as, (i) adhesive failure at the adhesive-adherend interface, (ii) cohesive failure within the adhesive layer,
and (iii) substrate failure within the adherend. Mixed-type, combination of these three classes can also occur [34]. Figure 1-5 schematically illustrates plausible failure types of adhesively bonded composite joints. Although the highest joint strength can be achieved by the substrate-type failure, the most commonly observed failure type in composite applications is one of the adhesive-type failures.

Figure 1-5  Sketches representing failure modes on adhesively bonded CFRP-joints (adopted from Ref. [34]).

Each type of failure results in a very unique fracture surface. For example, Figure 1-6 shows three different fracture surfaces, representing three types of failure modes. The failure mode is altered by different surface pre-conditions. For example, the adhesive type of failure is caused by the limited surface roughness of the adherend panels. While the mixed-type failure is achieved by the plasma pre-treatment of the adherend surfaces prior to the bonding step.
Figure 1-6 The fracture surfaces of double cantilever beam fracture test samples, prepared by using different surface pre-treatment procedures, which leads to different types of failures: (a) adhesive, (b) cohesive, and (c) mixed-type failure.

Interfacial Fracture Mechanics

The first study published on interfacial fracture mechanics appeared in 1959, where Williams [35] discovered the stresses around the crack tip possess two singularities: a square root singularity and an oscillatory square root singularity. Then, the development of interfacial fracture mechanism was mainly motivated by the multi-layered structures such as thin film/substrate material systems used in electronic devices and composite material systems used in aerospace structures. Especially, in late 1980s, Hutchison [36], Rice [37], and Evans [38] have significantly contributed to development of this field. The interfacial fracture mechanics problems have been usually approached by liner elastic fracture mechanics or cohesive zone modeling.
At the local scale, bond line mechanical response is typically characterized by a traction-separation curve (i.e. cohesive law), $\sigma = \sigma(\delta)$ as sketched in Figure 1-7.

Considering steady-state conditions, the area under this curve is defined as cohesive fracture energy (or work of separation per unit area), $\Gamma_0$, which is a toughness indicator. The cohesive law is regarded as a material property for each adhesive-adherend pair), and can be assumed to be independent from the adhesive layer thickness for a sufficiently thick layer [39]. Although the cohesive law is often regarded as a phenomenological model, the mechanisms of each deformation stage could be clearly identified. Under the low traction at the bond line arising from a typical service loads, the adhesive layer deforms elastically and the interface maintains intact. After the yield strength of the adhesive material, $\sigma_y$ is reached, the plastic deformation of the adhesive induces a large separation, where the surface traction increases with a relatively smaller rate. The increase of the traction is attributed to the combined effect of the increasing hydrostatic stress in the constrained tri-axial stress state, and the strain hardening of the adhesive. Finally, when the local traction exceeds the interfacial cohesive strength, $\tilde{\sigma}$, the adhesive layer debonds from the adherend substrate.

This energy dissipation process can only exist if the cohesive interface strength is greater than the adhesive yield strength ($\tilde{\sigma} > \sigma_y$). Otherwise, the plasticity of the adhesive layer can be shielded entirely, which is undesirable situation for bonding applications. In the other extreme, when the interface strength is even stronger than the ultimate strength of the adhesive material, crack propagates through the adhesive material rather than along the interface (cohesive type failure), even though the traction-separation law exhibits a similar shape with reinterpreted as the ultimate strength of the adhesive.
Therefore, the bond line toughness is strongly controlled by the adhesive mechanical properties. For example, increasing the yield strength (or hardening rate) would shorten the stage A-B on the traction-separation curve and lead to low ductility and even a sudden ductile-brittle transition when $\sigma_y > \dot{\sigma}$. On the other hand, both aging and environmental contaminants often lead to hardening of most polymer-based adhesives, accompanied with the degradation of interfacial strength, $\dot{\sigma}$. Both effects may considerably reduce the effective fracture toughness [39-41].

![Figure 1-7](image)

Figure 1-7  (a) Cohesive traction-separation law for the adhesive layer. (b) Sketch of the line bond separation, showing the different cohesive separation stages: (A) start of adhesive yielding, (B) interfacial debonding (damage initiation), and (C) full separation (fully damaged)

**Experimental Methods**

The mechanical testing of adhesively bonded structures can be categorized as (1) testing methods for bulk adhesive mechanical properties and (2) fracture testing of adhesive joints for interfacial fracture properties [2]. The first is required for proper characterization of mechanical properties of bulk adhesive and includes tensile, compressive and shear tests. The
Tensile mechanical properties are generally determined using bulk specimens according to ASTM D638-14 [42] or a thin layer between two steel bars as in the butt joints according to ASTM D2095-96 [43]. Figure 1-8(a) shows typical samples geometry for bulk specimens. The compressive tests use bulk specimens in various shapes. One of the commonly practiced testing standards for compressive properties of adhesives is ASTM D695-15 [44]. The compressive tests are usually less common to perform since compressive yield strength is normally assumed to be equal to tensile yield strength according to Von Misses model [2]. Similar to tensile test methods, the testing methods for shear properties use bulk and thin layer samples. The former includes bulk torsion test [45], notched plate shear method [46], while the latter includes butt joint under torsion [47], thick adherend shear test [48].

![Figure 1-8](image)

Figure 1-8 (a) Tensile samples for bulk properties. (b) DCB sample and testing procedure.

The fracture tests are also performed on bulk adhesives to determine the material fracture toughness based on linear elastic fracture mechanics approach. The common practice uses compact tension or single edge notch bend specimens to quantify mode-I fracture toughness of bulk adhesives according to ASTM [49]. It should be noted that, for all bulk testing methods, the major challenge with fabrication of bulk adhesive samples is formation
of excess voids during casting process, which can bias the measurements significantly. This has to be taken into consideration during data reporting.

Second, numerous attempts have been made to characterize interfacial fracture properties of adhesively bonded layered structures using varying sample geometries under wide ranges of mode-mixities [50-54]. In layered composite application, beam-like laminated specimens are preferred with their advantage of easy manufacturability and testing. The commonly used configurations in interfacial fracture experiments of adhesively bonded composite are: (1) the double cantilever beam (DCB) for mode-I fracture characterization [55], (2) the end notched flexure test (ENF) [56] and end-loaded split (ELS) test [57] for mode-II fracture characterization, and (3) the mixed-mode bending (MMB) test [58] for varying mode-mixity fracture characterization. Figure 1-8(b) depicts a typical DCB sample and its testing configuration.

**Numerical Methods**

The cohesive zone modeling (CZM) approach is one of the widely employed approaches to simulate the interfacial failure of adhesively bonded structures. The CZM is a phenomenological way to model the fracture process zone by representing the material behavior with the relation between the surface tractions and the relative displacement, namely the “traction-separation law”. With introduction of cohesive traction-separation behavior of the interface (or constitutive relationship), this approach facilitates to model interfacial fracture nucleation and growth, without dealing with drawbacks linear elastic fracture mechanics approach such as stress singularity. The concept of CZM was originated from the strip yield model, firstly introduced by Dugdale [59] and Barrenblatt [60, 61]. In general, the CZM constitutive relationships can be classified in two groups (i) non-potential
based models and (ii) potential based models. Over the past few decades, many researchers have proposed a variety of potential-based traction-separation laws for modeling different fracture behaviors (see for example the review article by Park and Paulino [62] and these references are therein).

![Figure 1-9 The bilinear traction-separation curve.](image)

The bilinear traction-separation law [63] has been one of the widely used model to study delamination failure of thin composites. Figure 1-9 shows the bilinear traction-separation curve, which is composed of linear elastic deformation, followed by a linear softening domain representing the progression of crack surface displacement till full separation. In the linear elastic part, the cohesive surface tractions \((t_n, t_s)\) and displacements \((\delta_n, \delta_s)\) are related to each other by initial (penalty) stiffness matrix, \(K\), as follows;

\[
\begin{bmatrix}
  t_n \\
  t_s
\end{bmatrix} =
\begin{bmatrix}
  K_{nn} & K_{ns} \\
  K_{sn} & K_{ss}
\end{bmatrix}
\begin{bmatrix}
  \delta_n \\
  \delta_s
\end{bmatrix}.
\]

(1)
Generally, no coupling between shear and tension is assumed ($K_{ns} = 0$). Within this domain, the cohesive surface linearly deforms until the tractions reach the critical traction values ($\hat{\sigma}_n, \hat{\tau}_t$). Thereafter, a linear softening will commence until reaching the critical separation values ($\hat{\delta}_n, \hat{\delta}_s$). Considering only either pure mode-I or mode-II fracture, the corresponding cohesive-traction-separation curve can be utilized without any consideration of mode-mixity. For example, in pure mode-I fracture, the maximum nominal traction criterion ($t_n \geq \hat{\sigma}$; $\hat{\sigma}$ critical normal traction) can be employed to initiate the damage. In addition, the damage evolution can be achieved when the mode-I driving fracture force reaches critical value ($\Gamma \rightarrow \Gamma_0$), wherein $\Gamma_0$ is the mode-I cohesive fracture toughness. However, in case of mixed mode fracture, the effective critical traction and cohesive fracture toughness have to be evaluated knowing the mode-mixity ratio [64, 65].

**Introduction: Intergranular Stress Corrosion Cracking**

Stress corrosion cracking (SCC) refers to the failure by cracking of engineering materials caused by the combined and synergetic interaction of mechanical tensile stress and corrosive reactions [66]. A wide range of high strength pipeline steels is vulnerable SCC. For example, 21 % of steel pipeline failures is attributed to SCC [67]. The critical aspect of SCC is the brittle failure of the ductile high-strength alloys, and the associated reduction of the fracture toughness. Typically, SCC initiates at localized corrosion sites such as surface discontinuities, pits and grain boundaries. The initiation and growth stages of SCC are significantly affected by environmental parameters. These parameters include, but not limited to, temperature, pH, pressure, solute species, solution viscosity. For example, the different
combination of potential and pH of the solution can alter the SCC mechanisms. Potential-pH diagrams are commonly used to determine the thermodynamics stability of phases of metals, thereby predict the SCC susceptibility of the material under the given environmental conditions. It should be noted that potential-pH diagrams can be biased by the deviation of the electrochemical conditions at the crack tip relative from that of the bulk solution.

![Figure 1-10 Material cross-sections of high strength steels, showing (a) intergranular SCC under high-pH conditions, (b) transgranular SCC under nearly neutral-pH conditions. (both images are magnified 250 times). (adopted from Ref. [69]).](image)

The pipeline SCC has been categorized into two main groups (1) high-pH SCC and (2) nearly neutral-pH [68, 69]. The former leads to a failure by intergranular SCC since grain boundaries are more susceptible for dissolution then the grain interior. However, the latter results in failure by intergranular SCC. Figure 1-10 illustrates typical crack growth paths for both intergranular SCC under high-pH conditions and transgranular SCC under nearly neutral-pH conditions. In addition to pH level, the potential has detrimental effect on the SCC mechanism. The potential range of maximum susceptibly to SCC can be determined by potential sweep measurements. For example, Figure 1-11 shows Schematic current-potential
curve showing range of maximum susceptibility to SCC for a steel in carbonate/bicarbonate solution for a fixed pH level. The maximum susceptibility to SCC is anticipated to occur within the active passive transition region in the curve [70].

In addition, metallurgical parameters such as alloying composition, microstructure, heat treatment have notable effects on SCC susceptibility of materials [68, 69]. For example, a low alloy steel can provide high resistance to SCC in carbonate-bicarbonate solution with enhanced molybdenum content [69]. In another scenario, it was shown that heat-treatment can alter the SCC type from transgranular to intergranular for austenitic stainless steels in chloride solutions [71]. SCC is also very sensitive to grain boundary precipitation in case of sensitization austenitic stainless steels. A preferential dissolution of depleted elements in the grain boundaries also affects the corrosion mechanisms [72].

![Schematic current-potential curve showing range of maximum susceptibility to SCC for a steel in carbonate/bicarbonate solution](image)

Figure 1-11 Schematic current-potential curve showing range of maximum susceptibility to SCC for a steel in carbonate/bicarbonate solution (Adopted from Ref. [70])
SCC is also referred as a delayed failure process, since the crack initiate and propagate a very slow rates ($\sim 10^{-9}$ m/s) until the crack driving force exceeds the material fracture toughness. In general, there are three distinct stages observed during SCC process. Figure 1-12 shows a schematic diagram of a typical SCC progression, the growth rate as a function of the crack tip stress intensity factor, highlighting the three regimes of crack propagation with different rates. The first stage is the SCC initiation stage and consists of chemical attack, chemo-mechanical interactions, and the slow growth (microstructural evolution of crack). Upon exceeding the threshold stress intensity factor for SCC, the crack undergoes a steady-state propagation with a plateau growth rate in the second stage. In the stage 3, the crack continues to propagate with the increasing growth rate and final failure occurs when the stress intensity factor reaches the material fracture toughness.

![Schematic diagram of a typical SCC evolution, logarithm of crack growth rate as a function of the crack tip stress intensity factor, showing three regimes of crack propagation with different rates.](image-url)
SCC mechanisms can be collected in two main groups: (1) anodic and (2) catholic mechanisms. In the former case, the active dissolution and removal of the material from the crack tip facilitates the crack growth under the constant tensile stress. In the latter case, the absorption of hydrogen atoms (produced by cathodic reduction of water molecules) in the material causes localized material property changes such as formation of a layer with enhanced dislocation mobility. Such localized plasticity could result in material embrittlement due to dislocation pile near by the edge of the plastic zone (HELP, hydrogen enhanced localized plasticity) [73]. The enhanced dislocation mobility nearby grain boundaries with presence of hydrogen atoms in 310 S stainless steel was shown by transmission electron microscopy (TEM) [74]. Figure 1-13(a) shows a composite TEM image of dislocation pile-up near by a grain boundary with (lighter lines) and without hydrogen (darker lines). The density of the dislocation pile-up near a grain boundary is increased by hydrogen ingress.

![Composite TEM image](image1.png)

Figure 1-13 (a) A composite transmission electron microscopy (TEM) image, showing the disalcaotion pile-up density near by a grain boundary with hydrogen atoms (lighter lines) and without hydrogen atoms (darker lines) in the material (Adopted from Ref. [74]). (b) Scanning electron microscopy images of fracture surface of hydrogen pre-charged single edge notch fracture X65 steel sample, highlighting surface micro/nano dimples associated with hydrogen-induced nano-void coalescence mechanisms (adopted from Ref. [77]).
In an alternative mechanism, hydrogen ingress can weaken atomic bonds between iron atoms, and thereby causes the cleave-like failure (HEDE, Hydrogen enhanced decohesion) [75]. Alternatively, hydrogen atoms in the vicinity of plastic process zone can promote accumulation of excess vacancy clusters and enables formation of nano-micro voids, which reduces the material ductility (MVC or NVC, micro or nano void coalescence) [76, 77]. For example, Figure 1-13(b) shows scanning electron microscopy images of fracture surface of hydrogen pre-charged single edge notch fracture X65 steel sample, where the mating surfaces exhibit clusters of nano-dimples. This surface features are attributed to formation of nano-voids due to presence of hydrogen, which causes quasi-brittle fracture.

There is widespread debate about the mechanism of SCC, including the contributions of mechanical vs. chemical processes in the initial damage percolation, leading to a macroscopic crack growth and the associated role of hydrogen embrittlement. Some of the widely recognized mechanistic models can be listed as follows: Corrosion tunnel model [78], adsorption enhanced plasticity model [79], film-induced cleave model [80], localized surface plasticity [81], surface mobility model [82]. Although numerous attempts have been made to deliver a mechanics-based model for SCC, there has not been a universal model providing a complete understanding of initiation and growth stages of SCC.

**Thesis Organization**

This thesis is a naive attempt to provide some physical and mechanical understanding of interfacial degradation mechanisms in two different problem sets. The first part, Chapters 2-5, examines the contamination-induced interfacial degradation mechanisms in polymer matrix composites. The second part, Chapters 6-9, focuses on the early stage degradation of
microstructure and mechanical properties in a pipeline steel undergoing high-pH intergranular corrosion in sodium bicarbonate solution. The thesis is composed of five published journal articles, and three manuscripts prepared for future publications.

Chapter 2 explores the probable correlation between degradation in bond line fracture toughness and the changes in the measurable mechanical properties of the adhesive layer arising from environmental contamination in adhesively bonded composite structures. The proposed framework utilizes the large scale bridging of interfacial fracture, which considers the significant contribution of plasticity on the macroscopic bond line fracture toughness. The study suggests that there is a scaling between the interfacial cohesive fracture toughness and the nanoindentation hardness. The scaling correlation has the potential to be utilized in assessing the relative trend between different contaminants. While the proposed scaling is verified for a common adhesive-adherend system in aerospace industry, with additional examination of other systems, the proposed scaling law might facilitate the utilization of the perceived non-destructively evaluated indentation hardness to serve as an indicator for the bond line macroscopic fracture toughness.

Chapter 3 examines the effect of environmental contamination level on the mode-I failure and fracture surface evolution of adhesively bonded composite joints. The study reveals an Arrhenius-type correlation between interface toughness and contaminant concentration was observed, with potential to predict the bond line toughness deterioration level. The study reveals that increasing the contaminant concentration changed the fracture surface morphology from ductile-to-brittle failure mode, driven by diminished plasticity within the adhesive layer. The study suggests that the bond line contamination deteriorates the interfacial toughness through two mechanisms: (i) weakening the interfacial bonding
strength, and thereby reducing the interfacial toughness, and (ii) shielding the plastic energy dissipation within the adhesive layer, and leading to a reduction in the overall effective bond line toughness.

Chapter 4 utilizes the principals of interfacial fracture mechanics and modified Gibbs adsorption equation to provide a predictive correlation for the macroscopic (effective) fracture toughness of polymer-based adhesive interfaces exposed to varying level of contaminant concentration. The modified Gibbs adsorption equation is utilized to correlate the contamination-induced degradation of the interfacial surface energy as a function of contaminant surface concentration. Interfacial fracture mechanics principals are applied to extend the correlation to the macroscopic fracture toughness of the interface.

Chapter 5 presents a linear correlation between the interfacial toughness and the resulting fracture surface roughness for a polymer-based interface. Statistical fracture surface analysis is performed by utilizing 1D height-height correlation function. The study suggests that the roughness exponent of the self-affinity is independent of the interfacial toughness, whereas the cut-off length scale of the self-affinity exhibits a linear correlation with varying the interfacial toughness. The observed correlation is attributed to the variation of the process zone size imposed by the altered interfacial fracture toughness. The presented correlation shows potential for the utilization of the statistical characterization of the fracture surfaces to estimate the interfacial toughness.

Chapter 6 focuses on morphology and mechanical stress evolution during high-pH intergranular corrosion (IGC) of X70 pipeline steel in sodium bicarbonate solution. It was found that IGC produces crevices at grain boundary triple junctions and triangular wedges of corrosion product around the triple junctions. Mechanical stress evolution during corrosion
was monitored using in situ stress measurements and related to internal oxidation within the IGC layer. Evidence was also presented for selective oxidation of silicon solute at grain boundaries during the early stages of intergranular attack.

Chapter 7 reports locally resolved ex situ nanoindentation measurements at corroded grain boundaries in X70 pipeline steel, in the pH and potential ranges of maximum SCC susceptibility. The measurements reveal evidence for degradation of hardness near grain boundaries. These are apparently the first observations of local corrosion-induced softening of grain boundaries under conditions associated with high SCC susceptibility.

Chapter 8 presents combined experimental and atomistic computational analysis of the grain boundary degradation in X-70 pipeline materials under active dissolution potentials at pH 8.2. The study suggests that (1) vacancies, rather than interstitial hydrogen-atoms, generated by intergranular corrosion promotes dislocation nucleation, which in turn, results in grain boundary degradation; and (2) the degradation level at grain boundaries is controlled by the vacancy concentration, varying with the relative distance to grain boundaries according to Fickian diffusion law.

Chapter 9 examines sub-surface mechanical degradation of an X70 pipeline steel generated by high-pH intergranular corrosion (IGC) in sodium bicarbonate solution. The continuous indentation measurements conducted within the IGC-affected layer exhibited 10% reduction in the indentation hardness, without a noticeable change in the elastic modulus. The indentation size effect study suggests that the observed reduction in the indentation hardness can arise from the reduction of the lattice resistance (Peierls-Nabarro stress). The reduced lattice resistance is attributed to clusters of atomic vacancies generated by the preferential dissolution of Si atoms within the IGC-affected layer. The present
experimental findings are anticipated to provide new insights for better mechanical understanding of intergranular corrosion and intergranular stress corrosion cracking.

Lastly, Chapter 10 provides an integrative summary and outlook.

References


CHAPTER 2. UTILIZATION OF NANOINDENTATION TO EXAMINE BOND LINE INTEGRITY IN ADHESIVELY BONDED COMPOSITE STRUCTURES

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Denizhan Yavas, Xu Shang, Wei Hong, Ashraf F. Bastawros
Department of Aerospace Engineering, Iowa State University, Ames, IA 50011-2271

Abstract

This study explores the probable correlation between degradation in bond line fracture toughness and the changes in the measurable mechanical properties of the adhesive layer due to environmental contamination in adhesively bonded composite structures. Nanoindentation technique is utilized to measure the adhesive Young’s modulus and hardness. The proposed framework utilizes the large scale bridging of interfacial fracture proposed by Tvergaard and Hutchinson (1994), for considering the significant contribution of plasticity on the macroscopic bond line fracture toughness. A typical adhesive-adherend material system (EA9394/Hexcel IM7-G/8552) exposed to different contaminants at the same concentration is examined. Hardness measurements showed two distinct effects of contamination on the adhesive material; namely (i) softening and (ii) hardening depending on the class of contaminants. In addition, macroscopic mode-I fracture toughness was independently measured by double cantilever beam test. Finite element method employing cohesive zone method was used to rationalize the experimental results and the prospective scaling-laws. The combined experimental results of macroscopic properties and the
numerical results of the interfacial properties showed the role of contamination in reducing the plastic dissipation within the bond line and the macroscopic deterioration of the bond line effective fracture toughness. The results showed the existence of a correlation similar to Tvergaard and Hutchinson’s results. However, the results suggest a scaling between the interfacial cohesive fracture toughness and the measurable flow stress. The scaling correlation has the potential to be utilized in assessing the relative trend between different contaminants. While the proposed scaling is verified for a common adhesive-adherend system in aerospace industry, with additional examination of other systems, the proposed scaling law might facilitate the utilization of the perceived non-destructively evaluated indentation hardness to serve as an indicator for the bond line macroscopic fracture toughness.

**Introduction**

Carbon fiber reinforced polymer (CFRP) composites have been extensively utilized as a major construction material in modern civil aircraft industry, because of their high strength-to-weight ratio. Adhesively bonded joints are extensively used with CFRP composites, with the advantages of high strength-to-weight ratio, uniform stress along the bond line, and design flexibility for assembly of complex airframe structures [1]. Reliability of bonded joints has been studied extensively by brute-force testing under many service environments, including: (i) service temperature [2, 3], (ii) moisture [4, 5], (iii) loading history (i.e. amplitude and frequency of dynamic loads) [6], (iv) thermal cycling [7, 8], (v) exposure to contaminants [9], and (vi) exposure to radiation [10]. The complex physical and chemical interplay between these factors may result in accelerated or delayed failure of the
bond line. The difficulty remains in setting a failure criterion or a threshold, similar to metallic structure wherein fatigue crack propagation is the major factor. The challenge remains in the early detection of the interfacial progressive damage of the bonded structures and the assessment of the current level of the effective interfacial fracture toughness, before the onset of a catastrophic failure.

This study explores a probable correlation between the contamination-induced degradation of bond line toughness and the degradation/changes in measurable mechanical properties of the adhesive layer, measured by indentation testing. Indentation testing can be thought of as a non-destructive evaluation procedure, wherein the residual indentation impression is of the same order as the surface roughness, and is much smaller than bond line thickness. The proposed framework employs the large scale bridging of interfacial fracture proposed by Tvergaard and Hutchinson [11], hereafter denoted TH, wherein plasticity has a major role in the toughness of the polymeric adhesively bonded joints (see for example Refs. [12, 13]). In TH-framework, the effective work of fracture per unit area on the interface, $\Gamma_{eff}$ is a function of the interfacial work of separation, $\Gamma_0$ and the yield strength $\sigma_y$ of the adhesive layer. The TH-framework suggests a dimensionless correlation between $\Gamma_{eff}$ and, $\sigma_y$ among other interfacial parameters. The current work examines the prospective of such scaling to be applied for comparative examination of a typical adhesive-adherend system exposed to different types of environmental contaminants at the same level of concentration, including typical hydraulic fluids and mold release agents. Mechanical properties including Young’s modulus, $E$, and hardness, $H$, of the adhesive layer were measured by nanoindentation technique. Macroscopic effective mode-I fracture toughness was measured by double cantilever beam (DCB) test. In addition, a cohesive-based finite element modeling
Proposed Hypothesis

Failure modes of adhesively bonded joints can be classified as, (i) adhesive failure at the adhesive-adherend interface, (ii) cohesive failure within the adhesive layer, and (iii) substrate failure within the adherend [14]. Although the highest joint strength can be achieved by the substrate failure mode, adhesive failure is the most common failure mode in composite applications [1]. The mechanical properties of the adhesive material play an important role on the joint strength [12, 13]. The mechanisms of deformation could be identified from the phenomenological traction-separation cohesive law, describing the bond line toughness.

Under steady-state conditions, the area under this curve is defined as cohesive fracture energy (or work of separation per unit area), $\Gamma_0$, which is a toughness indicator. The cohesive law is regarded as a material property (for each adhesive-adherend pair), and is not affected significantly by the thickness of the adhesive layer within the commonly used range of 100-300µm [15]. Typical service loads induce relatively low traction at the bond line, resulting in elastic deformation of the adhesive layer. After the yield strength of the adhesive material, $\sigma_y$ is reached, the plastic deformation of the adhesive induces a large separation, where the surface traction might increase slowly. The increase of the traction is due to the combined effect of the increasing hydrostatic stress in the constrained tri-axial stress state, and the strain hardening of the adhesive. Finally, when the local traction exceeds the

(FEM) was employed to rationalize the experimental results and the prospective scaling-laws, if any.
interfacial cohesive strength, $\hat{\sigma}$, the adhesive layer debonds from the adherend substrate. Such an energy dissipation process can only exist if the cohesive interface strength is greater than the adhesive yield strength ($\hat{\sigma} > \sigma_y$). Otherwise, the plasticity of the adhesive layer can entirely be shielded, which is an undesirable situation for an efficient bonding application. In the other extreme, when $\hat{\sigma} \gg \sigma_y$, crack propagates through the adhesive material rather than along the interface. Thus, it can be argued that the bond line toughness is directly correlated with the adhesive mechanical properties. For example, increasing the yield strength (or hardening rate) would lead to low ductility and even a sudden ductile-brittle transition when $\sigma_y > \hat{\sigma}$. In practice, both aging and environmental contamination often lead to hardening of most polymer-based adhesives, accompanied with the degradation of interfacial strength. Both effects typically reduce the bond line fracture toughness.

The measured mechanical properties of the adhesive, $\sigma$, and $E$, can be correlated to the measured fracture energy, $\Gamma_{\text{eff}}$, through the following argument. $\Gamma_{\text{eff}}$ can be written as the confluence of the interfacial cohesive (surface or binding) energy $\Gamma_0$ and the energy dissipation through plastic (or inelastic) deformation, $W_p$, such that

$$\Gamma_{\text{eff}} = \Gamma_0 + W_p \quad (1)$$

For a bond line thickness $h$ greater than $R_0$, which is a material-based length scale, TH showed that $\Gamma_{\text{eff}}$ becomes independent of the bond line thickness. $R_0$ is approximately the plastic zone size as long as $R_0 < h$. When $\Gamma_{\text{eff}} > \Gamma_0$ for large scale bridging, the plastic zone size scales with $R_0$. When plasticity has negligible contribution and the crack propagate
at the interface at constant applied stress intensity factor, $K = K_0$; $R_0$ is defined as a reference length scale,

$$R_0 \equiv \frac{1}{3\pi} \left( \frac{K_0}{\sigma_y} \right)^2 = \frac{1}{3\pi(1-\nu^2)} \frac{E \Gamma_0}{\sigma_y^2}.$$  \hspace{1cm} (2)

Here, the Young’s modulus $E$ and Poisson’s ratio $\nu$ are the properties of the bond line material. A measure of $W_p$ (per unit bond line width) can be estimated from the strain energy density (scales with $\sigma_y^2/E$) and the size of the process zone (scales with $R_0^2$) such that,

$$W_p \sim \frac{\sigma_y^2}{E} (R_0)^2 \sim \frac{E \Gamma_0^2}{\sigma_y^2}.$$  \hspace{1cm} (3)

The presented scaling in Eq. 3 suggest strong influence of $\sigma_y$ compared to $E$.

Additionally, while not intuitively, $W_p$ is a function of $\Gamma_0$. Accordingly, Eq. 1 becomes,

$$\Gamma_{\text{eff}} = \Gamma_{\text{eff}} (\Gamma_0, \sigma_y, E).$$  \hspace{1cm} (4)

For a wide range of material properties TH showed that for adhesive layer thickness $h/R_0 > 4$, full plasticity enhancement of toughness is reached. At such adhesive layer thickness, the numerical results of TH, summarized on Figure 2.1 show the prospective form of Eq. 4 as a scaling of $\Gamma_{\text{eff}}/\Gamma_0$ with $\hat{\sigma}/\sigma_y$ for a broad range of $\hat{\sigma}/\sigma_y$ ratio. For a known intrinsic fracture parameters of the interface ($\Gamma_0$ and $\hat{\sigma}$), the observed trend on Figure 2.1 might be interpreted as a prospective correlation between $\Gamma_{\text{eff}}$ and $\sigma_y$. One might argue about the existence of a range, typically $\hat{\sigma}/\sigma_y \leq 4$, wherein interfacial plastic dissipation has a noticeable role in increasing the $\Gamma_{\text{eff}}/\Gamma_0$ ratio, with no significant dependence on the
hardening exponent, \( N \). Additionally, at the early stage of \( \hat{\sigma}/\sigma_y \approx 2 \), \( \Gamma_{\text{eff}} \) is of the same order of \( \Gamma_0 \). This is similar to the scenario of interface embrittlement and reduced role of plasticity, arising from contaminated bond line.

![Figure 2-1](image)

**Figure 2-1** (a) Summary of TH numerical results (Fig 8, Ref. [11]), showing the correlation between the ratio of the effective work of fracture per unit area to the interfacial work of separation, and the ratio of interfacial cohesive strength to the yield strength of the adhesive layer for two different hardening exponent. (b) Geometry of the bond line joint.

In the proposed experimental framework, we will be looking for a similar correlation, wherein \( \Gamma_{\text{eff}} \sim \left(1/\sigma_y\right)^m \) for the practical range of \( 0.5 \leq \hat{\sigma}/\sigma_y \leq 2 \) observed in the current degradation study. To explore such relation, \( \Gamma_{\text{eff}} \) and \( \sigma_y \) should be independently measured. Here, the Tabor approximation [16, 17] is being utilized for the indentation hardness to be considered as an average measure of the material yield strength in compression (\( H \sim 3\sigma_y \)).
$\Gamma_{eff}$ will be measured experimentally from DCB tests. The intrinsic fracture toughness properties will be examined numerically to match the experimental measurements $\Gamma_{eff}$ and the peak load of the force-displacement curve of the DCB sample. Once these correlations are established, we anticipate that a contamination induced softening within the adhesive layer might result in the increase of $\Gamma_{eff}$. With the aid of such correlations, the measured $E$ and $H$ of the adhesive material may provide the relative trends for $\Gamma_{eff}$, unless being overshadowed by significant reduction of $\hat{\sigma}$ that may embrittle the adhesive-adherend interface.

**Material and Sample Preparation**

**Adhesive Material and Contaminant Types**

Loctite Hysol EA9394 two-part epoxy was selected, as one of the commonly utilized epoxies in aerospace applications. This adhesive exhibits high toughness and strength even at a high operating temperature of 350°F (177°C) for the aviation industry, and can be cured at room temperature. Since the epoxy has aluminum powder fillers, care was taken during nanoindentation measurements in order to precisely probe the adhesive properties away from the surrounding fillers [18]. A variety of environmental contaminants, including three different types of aviation hydraulic fluids and two different types of mold release agents were adopted in this study. These two groups of contaminants are commonly observed in service and repair environments. The contaminant types are tabulated in Table 1. A controlled contamination surface concentration of 55$\mu$g/cm$^2$ was applied, which represents non-volatile residue cleanliness of Level-J according to Military Standard 1246C [19].
Table 2.1  Different classes of contaminants used in this study.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Description</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HF-1 MIL-PRF-87257</td>
<td>Aviation hydraulic fluid</td>
</tr>
<tr>
<td>2</td>
<td>HF-2 SAE AS1241</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>HF-3 MIL-PRF-85570</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>F-44 LOCTITE FREKOTE 44-NC</td>
<td>Mold release agent</td>
</tr>
<tr>
<td>5</td>
<td>F-700 LOCTITE FREKOTE 700-NC</td>
<td></td>
</tr>
</tbody>
</table>

**Sample Preparation**

Nanoindentation samples consist of a contaminated layer of the adhesive on top of a glass slide. The selected contaminants were first diluted by a volatile agent such as hexane at the proper concentration, then the diluted solution was applied uniformly on top of the uncured adhesive layer. The desired surface concentration was controlled by the height of the solution, and verified by performing infra-red spectroscopy to be within few percent. Finally, the samples were cured in a furnace at 190°F (88°C) for 2h according to Hysol EA9394 material data sheet.

The fracture DCB samples consist of two adherend composite panels bonded to each other by a layer of Hysol EA9394 adhesive. Adherend panels with a layup of $[\pm 45^\circ, 0^\circ]_s$, were constructed by stacking 10 plies unidirectional prepregs (Hexcel IM7-G/8552) and two additional plies of bi-directional weaved fabric (Hexcel W3B-282) at ±45° on top and bottom sides. Standard fabrication of vacuum bagging and hot-press curing methods were implemented. The adherend panel surfaces were grit blasted to induce 4-5 μm surface roughness, which is generally considered as sufficient surface roughness for a proper adhesion process [20]. After the sand-blasting process, the panel surfaces were cleaned by
water and hexane, then the panels were left in a drying furnace at 160°F (71 °C) for 2h with a heating and cooling rates of 5°F/min, following NAVAIR 01-1A-21 (see Sec. 6-7a (2)) technical manual [21].

![Diagram of double cantilever beam specimen geometry](image)

Figure 2-2  Double cantilever beam specimen geometry.

The diluted contaminants were uniformly applied on the roughened and cleaned surface of the composite panels. Finally, a pair of exposed/unexposed adherend panels were bonded to each other by an adhesive layer. A 125μm thick Teflon film was used to create an initial crack at the edge of the samples. In addition, a 250μm shim was inserted at the edges to control the adhesive layer thickness. The resulting bond line thickness was measured to be around 400μm. Finally, bonded composite panels were cured under 5psi (34.5kPa) pressure at room temperature (22 °C) for 16 hrs. Subsequently, another final rapid curing process was performed in the furnace at 190°F (88°C) for 2h. These assembled composite panels were cut
into sample dimensions (25.4mm x 180mm) and steel loading blocks were glued to the ends of the samples. Figure 2.2 shows the sample geometry and dimensions.

**Hardness Measurements by Nanoindentation**

Nanoindentation is utilized to probe the changes in mechanical properties of the adhesive material due to contamination. Environmental contamination exhibited shallow and non-uniform adsorption/diffusion into the adhesive polymer network. Thus, nanoindentation technique is more suitable to probe such subtle changes near the adhesive surface, rather than bulk property testing. All indentations were performed in force control using the Hysitron TI 950 TriboIndenter. A trapezoidal loading profile, which consists of a 5s linear loading, 2s hold at the peak load, and 5s linear unload, was utilized to impose the regular patterns of nano-indentation using a Berkovich tip with a tip radius of about 150 nm. Several indentations were performed on each sample with a peak load ranging from 1000µN to 6000µN with 1000µN intervals, which resulted in contact depths up to 5µm. Data analysis method proposed by Oliver and Pharr [22] was utilized to determine the indentation hardness, \( H \), and modulus, \( E \).

Figures 2-3 and 2-4 show the variation in indentation-measured \( E \) and \( H \) for different types of contaminants, respectively. It should be noted that these measured values should not be mistaken with the bulk macroscopic values, especially the hardness as it might display a size dependent response at the nano-scale [23]. Therefore, the percentage change with respect to the reference measurement are utilized in the comparison and also presented on Figures 2-3 and 2-4. \( E \) was found to vary within 10% of the reference value with no
identifiable trend with the contaminant type. On the other hand, two distinct effects of contamination on $H$; namely softening and hardening were observed depending on the contaminant group. For the examined adhesive, $H$ is decreased by the hydraulic fluid contaminants (softening of the adhesive), whereas it is increased by the mold release agent contaminants (hardening of the adhesive). According to our hypothesis, $\Gamma_{\text{eff}} \sim \left(\frac{1}{H}\right)^m$ for $\dot{\sigma} > \sigma_y$. If the hypothesis holds, the nanoindentation results predict higher degradation in bond line toughness in case of contamination by mold release agents (accompanied with hardness increase) compared to hydraulic fluids (accompanied with hardness reduction). Such prediction will be verified by the DCB tests.

Figure 2-3  Role of different contaminants on the measured indentation modulus. Error bars correspond to ±STDEV.
Figure 2-4  Role of different contaminants on the measured indentation hardness. Error bars correspond to ±STDEV.

**Mode-I Fracture Toughness Measurements by Double Cantilever Beam Test**

Bond line fracture toughness was measured by DCB test, according to ASTM-D5528-13 [24], for mode-I fracture characterization of adhesively bonded structures. All DCB tests were performed in displacement control at a loading rate of 0.02 mm/s using an INSTRON 8862 servo-electric computer controlled testing frame. Force, cross-head displacement and in-situ digital images of the crack growth were recorded simultaneously. Elaborate discussion
of the experimental details and measurement of the instantaneous crack tip position can be found in Ref. [25]. Mode-I energy release rate was calculated using modified beam theory,

\[ G = \frac{\alpha_1}{\alpha_2} \frac{3P\delta}{2ba} \]  

(5)

where \( P \) is the applied force, \( \delta \) is the cross-head displacement, \( \alpha \) is the instantaneous crack length, measured from the loading pin center to the current crack tip position, and \( b \) is the sample width, as indicated on Figure 2-2. The coefficients, \( \alpha_1 \) and \( \alpha_2 \) are dimensionless correction coefficients for finite displacement and change of the effective sample stiffness [26].

![Figure 2-5](image)

Figure 2-5  (a) Force-displacement curves and (b) derived fracture energy release rate curves, obtained from DCB experiments, along with the numerical results (dashed lines) for the examined cases.

Three DCB tests were performed for each class of contaminants. A representative set of force-displacement curves obtained from testing of reference (unexposed), HF-1, HF-3, and F-44 contaminated samples are presented in Figure 2-5(a), along with the FEM results (dotted line, discussed in Numerical Modeling Section). The slight change in the initial
loading stiffness arises from the differences in the initial crack length, $a_0$, being determined after an initial loading/unloading cycle to sharpen the manufactured interfacial crack-tip. The uncontaminated reference case has shown extended nonlinearity on the force-displacement curve (about one fourth of the loading level) before the start of the crack propagation. To the contrary, all contaminated cases have shown a linear increase up to the onset of crack propagation. This is the first evidence of the shielding of plasticity within the bond line. Upon reaching the maximum load carrying capacity of the joint, a progressive drop in the load is observed as a function of successive crack propagation. The associated zig-zag pattern is attributed to the intermittent propagation and arrest of the interfacial crack or relaxation of the fracture energy, followed by building up of the fracture driving forces. The corresponding derived mode-I energy release rate curves and the corresponding FEM results are presented in Figure 2-5(b), and clearly show the arrest and propagation of the crack for the reference case. However, the crack propagation is quite steady for the contaminated cases. This could be attributed to the absence of the plastic process zone within the bond line. In addition, it could be argued that propagation and arrest of the crack in the reference case is due to the reestablishment and collapse of the plastic process zone, within the bond line.

Figure 2-6 summarizes the experimentally measured average steady state levels of energy resale rate curves. All contaminant cases show significant reduction of the adhesive fracture toughness. The different hydraulic fluid contaminants show a drop of about 4-6 times the reference value. The mold release agent contaminants show more than an order of magnitude drop in the fracture toughness. For the reference case, the optical image insert shows a mixed failure mode between the adhesive and adherend, exposing the fibers within
the adhesive layer. All other contaminant cases at the reported level of contamination show adhesive failure mode.

![Graph showing effective fracture toughness measurements](image)

Figure 2-6  Summary of effective fracture toughness measurements for the examined cases at the same level of contamination concentration (55 µg/cm²), highlighting the severe chemical degradation of the adhesive strength, inserts show optical images of the fracture surfaces of the reference (uncontaminated) and HF-1 contaminated cases.

The DCB fracture toughness results show some consistency with the hardness measurements as an overall trend of Figure 2-4. For example, the mold release agent contaminants show increased hardness compared to the hydraulic fluid contaminants. Thus they should have lower level of fracture toughness compared to the reference and the hydraulic fluid contaminants. The hydraulic fluid contaminants show a drop in their hardness on Figure 2-4, which should have been manifested as an increase in the fracture toughness.
To the contrary, the group of the hydraulic fluid contaminants shows drop in their fracture toughness compared to the reference case. Though, they are 2-5 times higher than the mold release agent contaminants fracture toughness level. Additionally, the fracture toughness changes relative to each other in the same trend noted in Figure 2-4, though not with the same magnitude.

![Figure 2-7](image)

Figure 2-7  Correlation between experimentally measured effective bond line fracture toughness and bond line indentation hardness. All results are normalized by those of HF-1 contaminated case.

Figure 2-7 presents a summary of the experimental measurements to explore the relation between $\Gamma_{\text{eff}}$ and $H$. The values of HF-1 are utilized for normalization. A clear correlation can be identified among the contaminated cases, showing a strong influence of
the hardness (or yield strength) on the measured bond line toughness. The experimentally measured correlation exponent is around $m \approx 6.25$. Additionally, $\Gamma_{eff}$ for the reference is at least an order of magnitude above this correlation. Such discrepancies can be understood in view of Eq. 3, wherein $\Gamma_{eff}$ depends on both $\Gamma_0$ and $\sigma_y$. This set of measurements might suggest that $\Gamma_0$ is almost of the same order for all contaminated cases, but very different for the reference case. Accordingly, an experimental correlation of the type $\Gamma_{eff} \sim (1/H)^m$ can be identified for the contaminated cases, such that

$$\frac{\Gamma_{eff}}{\Gamma_{ref}} = \lambda \left( \frac{H}{\bar{H}} \right)^m. \quad (6)$$

Here $\Gamma_{eff}$ and $\bar{H}$ are the properties of a reference state, which could be one of the contaminated cases but having a similar order of magnitude for the cohesive properties. For the examined adhesive-adherend system and the diverse range of contaminants, $\lambda \approx 0.95$ and $m \approx -6.25$. This correlation will be further explored through numerical modeling, discussed next.

**Numerical Modeling**

**Computational Model**

Incorporating surface-based cohesive elements in FEM is one of the widely employed approaches to simulate the failure of adhesively bonded structures [27]. A bilinear traction-separation law [28] is employed to model the bond line failure, Figure 2-8. It is composed of linear elastic deformation, followed by a linear softening domain representing the
progression of crack surface displacement till full separation. For Mode I loading, the initial cohesive surface tractions, $t_n$ is related to the separation displacement, $\delta_n$ through an initial stiffness, $K_{nn} \approx \beta \left( E_l/h \right)_{\text{adhesive}}$ taken to be proportional to the ratio between the modulus and the thickness of the adhesive layer. Here $\beta$ is a constant much larger than unity, and is recommended to be around $\beta \approx 50$ [29]. Accordingly, the cohesive surface will undergo linear elastic deformation until it reaches the critical traction $\hat{\sigma}$. Thereafter, a linear softening will commence until reaching the critical separation $\hat{\delta}_n$. Since DCB test is a pure mode-I fracture testing, a maximum nominal traction criterion $(t_n \geq \hat{\sigma}; \hat{\sigma}$ critical normal traction) is employed to initiate the damage. Complete surface separation commences when mode-I driving fracture forces reaches critical value $(\Gamma \rightarrow \Gamma_0)$, wherein $\Gamma_0$ is the area under the traction separation curve.

Figure 2-8 The utilized bilinear traction-separation law, showing self-similar scaling approach to model degradation.
Numerical simulations were performed using the commercial FEM package SIMULIA Abaqus 6.12-2. DCB sample geometry was modeled using 2-D 4-node quadrilateral linear plane strain elements (CPE4). A single layer of cohesive surfaces was introduced at one of the adhesive-adherend interfaces to simulate interfacial crack propagation, whereas the other one was assumed to be perfectly bonded. Mesh was refined in front of the crack tip along the cohesive interface. Refined element length of 0.1 mm was used so that at least 3 elements exist within the CZ [29]. The adhesive layer was 400\(\mu\)m thick, with uniform square elements. The model was loaded to the corresponding crack root opening displacement, reached in the experiment.

Adherend composite panels were effectively modeled as an isotropic elastic material, whereas the adhesive layer was modeled as an isotropic elastic-plastic material. The effective flexural stiffness of the adherend material was derived from four point bend test according to ASTM-D7264/D7264M-07 [30] and was estimated to be \(E = 64\, \text{GPa}, \nu = 0.3\). The mechanical properties of the adhesive were \(E = 4.3\, \text{GPa}, \sigma_y = 69\, \text{MPa}, \nu = 0.43\) [31] with modest hardening exponent of \(n = 1/N \approx 6.2\) according to Ramberg-Osgood model [32]. The hardening exponent was evaluated by the ratio, work/complementary work for the range of interest (up to 3.5% strain) of the stress-strain curve of the adhesive material, reported by Guess et al. [31]. The two parameters \(\Gamma_0\) and \(\dot{\sigma}\) of the bilinear traction-separation law were calibrated by matching the peak force of the experimentally measured force-displacement curve [33]. Then, \(\Gamma_0\) was varied by scaling the linear softening domain while keeping its slope constant so that the traction-separation law remains self-similar as shown in Figure 2-8. Such variability can impose the scalability between interfacial fracture toughness and
interfacial cohesive strength, such that $\Gamma_0 - \hat{\sigma}^2$. While other scaling could have been implemented, however scaling both $\hat{\sigma}$ and $\hat{\delta}_n$ to keep the self similarity of the traction-separation law resulted in the best match of the experimentally measured maximum force for all DCB tests under different contamination conditions. The resulting energy release rate, calculated on a contour enclosing the crack tip, was compared to the effective fracture toughness, $\Gamma_{\text{eff}}$ evaluated from the experiment as shown on Figure 2-5 for reference and all contaminated cases. For the reference case, $\Gamma_{\text{eff}}$ was almost three times $\Gamma_0$ due to the large level of plastic work within the bond line. The typical discrepancies between the predicted and measured values of $\Gamma_{\text{eff}}$ were within few percent.

Table 2.2  Calibrated CZ parameters and measured yield strength for the reference and all contamination cases.

<table>
<thead>
<tr>
<th></th>
<th>Reference</th>
<th>HF-3</th>
<th>HF-2</th>
<th>HF-1</th>
<th>F-700</th>
<th>F-44</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{nn}$ (N/mm$^3$)</td>
<td>3 x 10$^6$</td>
<td>3 x 10$^6$</td>
<td>3 x 10$^6$</td>
<td>3 x 10$^6$</td>
<td>3 x 10$^6$</td>
<td>3 x 10$^6$</td>
</tr>
<tr>
<td>$\hat{\sigma}$ (MPa)</td>
<td>135</td>
<td>76</td>
<td>55</td>
<td>50</td>
<td>44</td>
<td>40</td>
</tr>
<tr>
<td>$\Gamma_0$ (J/m$^2$)</td>
<td>250</td>
<td>80</td>
<td>41</td>
<td>34</td>
<td>27</td>
<td>21</td>
</tr>
<tr>
<td>$\sigma_y$ (MPa)</td>
<td>69</td>
<td>61</td>
<td>62</td>
<td>66</td>
<td>72</td>
<td>74</td>
</tr>
</tbody>
</table>

Comparison with Experiment

The numerical simulation was utilized to understand the observed trend of the DCB measured fracture toughness and contrast with the corresponding nanoindentation
measurements for $\sigma_y$ and $E$. The corresponding $\Gamma_0$ and $\hat{\sigma}$ were varied to match the experimentally measured force-displacement, Figure 2-5(a), and energy release rate-crack extension, Figure 2-5(b), curves. Summary of the utilized CZ parameters are reported in Table 2.2, along with the experimentally measured $\sigma_y$ for the examined cases. It should be noted that $\Gamma_{\text{eff}}$ reaches $\Gamma_0$ for some of the worst contaminant cases, which is an indication of absence of plasticity at the interface. Qualitatively, the numerical simulations reproduced the experimentally measured trends in terms of matching maximum failure load and the steady-state energy release rate values. Though the numerical prediction did not exhibit the intermittent propagation and arrest of the interfacial crack. To capture such effect, the analysis must account for the inertial effects as well as the stochastic distribution of defects, which are beyond the scope of the current study.

Figure 2-9 provides a numerically derived map for the role of different cohesive properties on the interfacial fracture toughness of the bond line, mapped to the mechanical properties of one of the contaminants. There is about three fold or more drops in $\Gamma_0$ for the contaminated cases, compared to the reference state. $\Gamma_0$ also exhibited the same order of magnitude for the range of contaminants. With the progress drop in $\Gamma_0$, the amount of plastic work that could be dissipated within the adhesive layer is progressively deteriorating as well. Additionally, $\hat{\sigma}$ started to reach $\sigma_y$ and for the range of comparison it dropped below $\sigma_y$ for some of the contaminants. Accordingly the interface would decoher before the bond line can reach the state of plastic work dissipation. In other words, degradation of the critical cohesive traction due to contamination shields the plasticity within the adhesive material.
Figure 2-9  Summary of the numerical results for $\Gamma_{\text{eff}}$ with sets of $\Gamma_0$ and $\dot{\sigma}$, mapping the experimental cases.

Figure 2-10 summarizes the parametric numerical study to show the interplay between the interface fracture properties, and the role of the interface ductility on $\Gamma_{\text{eff}}$. The properties of HF-1 contamination are used for normalization. The computational trend shows that for constant cohesive properties, the flow stress or the hardness of the adhesive has a very limited effect on $\Gamma_{\text{eff}}$. However, it can be seen that the experimental data set transcend across multiple groups of different interface properties, and thereby the measured hardness exhibits stronger effect on $\Gamma_{\text{eff}}$. These results support Eqns. 3 and 4 that $\Gamma_{\text{eff}}$ is influenced by both $\Gamma_0$ and $\sigma_y$. 
Figure 2-10: Summary of numerical study showing the interplay between the cohesive parameters and the bond line yield strength on the effective fracture toughness. The experimental data (filled symbols) transcends across multiple groups of interface properties. All results are normalized by those of HF-1 contaminated case.

**Numerically Augmented Experimentally Derived Scaling**

The experimentally measured $\Gamma_{\text{eff}}$ and $\sigma_y$ along with the numerically derived interface properties ($\Gamma_0$ and $\hat{\sigma}$) are presented in Figure 2-11 in a dimensionless correlation of $\Gamma_{\text{eff}} / \Gamma_0$ with $\hat{\sigma} / \sigma_y$, similar to that shown by TH and presented in Figure 2-1. Despite that these four quantities are derived from two independent tests and numerical simulation fitting.
the macroscopic response, a “weak” scaling could be observed between these two ratios of interface toughness vs. interface strength for the extended range of the examined contaminants. While TH have shown the ratio $\Gamma_{\text{eff}} / \Gamma_0$ to be of order unity for this range of $\dot{\sigma} / \sigma_y$, the current simulation show this ratio to be in the order 2.5-3. With such weak scaling ($m \approx 0.08$), an experimental procedure might be suggested for evaluating the intrinsic interface fracture properties as a result of exposure to environmental contamination. Though additional experimental data sets are required to set the statistical limits of such correlation.

Figure 2-11 Correlation between the ratio of effective fracture toughness to calibrated interfacial cohesive toughness and the ratio of interfacial cohesive strength to yield strength for $\Gamma_{\text{eff}}$ and $\sigma_y$ measured experimentally, while $\Gamma_0$ and $\dot{\sigma}$ calibrated numerically on logarithmic scale.
To this end, there is a subtle difference between the experiments and the numerical simulation. The experimental data in Figure 2.7 suggested a strong correlation between $\Gamma_{\text{eff}}$ and $\sigma_y$ in the form of Equation 6. However, the numerical results of Figure 2.10 suggest a weak correlation between these two quantities for constant cohesive parameters. Though Figure 2.9 and Equation 4 suggest a scaling between $\Gamma_0$ and $W_{\rho}$ for the examined adhered-adhesive system and for the explored domain of experiment. Physically, $\Gamma_0$ should be controlled by the chemical interaction between the adhesive layer and the contaminants. Though this correlation implies the possibility of $\Gamma_0$ scaling with $H$.

Figure 12 explores such prospective correlation between the experimentally measured hardness and the numerically calculated interfacial work of adhesion $\Gamma_0$, normalized with the properties of HF-1 contaminated case. A strong correlation could be identified, clearly showing the effect of contamination on deteriorating the interface properties. Such correlation could be rationalized in a power law correlation such that,

$$\frac{\Gamma_0}{\bar{\Gamma}_0} = \lambda \left(\frac{H}{\bar{H}}\right)^m. \quad (7)$$

Here $\bar{\Gamma}_0$ and $\bar{H}$ are the properties of a reference state, which could be one of the contaminated cases but having a similar order of magnitude for the cohesive properties. For the examined adhesive-adherend system and the diverse range of contaminants, $\lambda \approx 1.13$ and $m \approx -4.8$. 
The implication of Equation 7 is far reaching as it correlates the macroscopically measured hardness to the intrinsic state of cohesion, $\Gamma_0$. Accordingly, the correlations represented by Equations 6 and 7 provide a methodology to estimate the both the macroscopic ($\Gamma_{\text{eff}}$) and microscopic ($\Gamma_0$) characteristics of interface fracture for a contaminated case, through the bond line hardness measurement and the knowledge of the fracture properties for other cases of the same material system and bond line geometry ($h/R_0 > 4$).
These two correlations have far reaching significance for inspection of adhesively bonded joints. They could be used for comparative study to map the role of contamination on the effective fracture toughness of bonded joints. Though, it should be noted that the correlation between $H$ and $\Gamma_0$ is material dependent and is governed by the details of chemical effects of the contaminants on the molecular binding energy of individual polymers. Accordingly, similar correlations have to be derived for other adhesive-adhered material systems. Moreover, the interface topology and geometric roughness have a major role in changing the effective fracture toughness of the bond line [20]. Thus, it is essential to maintain geometric similarity between adhesive surfaces and their preparation methods in order to generalize the proposed correlations.

Conclusion

The presented study showed the potential of nanoindentation technique to predict the bond line fracture toughness by monitoring changes in the measurable mechanical properties of the adhesive material due to contamination. All examined contamination cases have shown marked macroscopic deterioration of the effective fracture toughness of interface, by limiting the energy dissipation through plastic deformation within the bond line. The combined experimental and simulation results suggest a scaling for both the effective fracture toughness and the interfacial cohesive fracture toughness, with the measured hardness of the adhesive layer. The proposed scaling law utilizes mechanical properties of the adhesive layer to elucidate the trends of the macroscopic fracture toughness for a common adhesive-adherend system in aerospace industry under different environmental exposures. The
proposed scaling law has the potential to facilitate the nanoindentation technique for
inspection of adhesively bonded joints for a wide range of material system. It could be
utilized to provide a comparative map of the role of contamination on the effective fracture
toughness of bonded joints.

References


25. Yavas D, Shang X, Bastawros AF. Role of contamination on bond line integrity of adhesively bonded composite joints, (manuscript to be submitted).


CHAPTER 3. MODE-I FRACTURE TOUGHNESS AND SURFACE MORPHOLOGY EVOLUTION FOR CONTAMINATED ADHESIVELY BONDED COMPOSITE STRUCTURES

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Denizhan Yavas, Xu Shang, Ashraf F. Bastawros
Department of Aerospace Engineering, Iowa State University, Ames, IA 50011-2271

Abstract

This study explores the effect of environmental contamination level on mode-I failure and fracture surface evolution of adhesively bonded composite joints. We examined a common adhesive/adherend material system (Hysol EA9394/Hexcel IM7-G/8552) exposed to a typical aviation hydraulic fluid (MIL-PRF-87257) at varying contaminant concentrations. The macroscopic bond line fracture toughness measurement by double cantilever beam test exhibited a progressive deterioration with increasing contaminant concentration. Even a trace level (3 µg/cm²) resulted in a 15% reduction of average bond line strength and 30% drop in bond line toughness. An Arrhenius-type correlation between interface toughness and contaminant concentration was observed, with potential to predict the bond line toughness deterioration level. Increasing the contaminant concentration changed the fracture surface morphology from ductile-to-brittle failure mode, driven by diminished plasticity within the adhesive layer. Finite element method employing cohesive
surfaces was also utilized to rationalize the experimentally observed trends. The combined experimental and numerical results suggest that the bond line contamination deteriorates the interfacial toughness through two mechanisms: (i) weakening the interfacial bonding strength, and thereby reducing the intrinsic interfacial toughness, and (ii) shielding the plastic energy dissipation within the adhesive layer, and leading to a reduction in the overall effective bond line toughness.

**Introduction**

Adhesively bonded carbon fiber reinforced polymer (CFRP) composite joints have been extensively utilized in the aerospace industry, with the advantage of a high strength-to-weight ratio [1-3]. They are very promising alternatives to traditional mechanical joints such as rivets and fasteners, commonly used in metal bonding applications. The application of traditional mechanical joining techniques to composite materials results in fiber cuts accompanied with stress concentrations and reduced structural integrity [3]. The introduction of adhesive joining has resolved many of these issues, with the advantages of more uniform stress transfer along the bond line and design flexibility for assembly of complex airborne structures. However, adhesive joints have not been efficiently used due to the lack of comprehensive material models with fatigue-like or damage evolution failure criterion [3]. As a result, adhesive joints are over-designed with the inclusion of mechanical fasteners as additional safety precautions. Additionally, environmental exposures have a detrimental effect on the mechanical performance and long-term reliability of the entire bonded structure [1, 2]. In practice, exposure to environmental contamination represents one of the major
technical challenges for subsequent composite repair, with stringent requirements for surface preparation and cleaning [4, 5]. Such effect is the focus of this study.

The structural reliability of adhesively bonded joints has been broadly studied under a wide range of environmental exposures, including service temperature [6-11], moisture [9-13], chemical contaminants [9, 14-16], and radiation [17]. In addition, the effect of harsh environmental conditions such as hydrothermal or chemical on the mechanical and physical properties of polymer-based adhesives was extensively studied [18-22]. The degradation process typically occurs through hydrolysis, oxidation, and dehydration reactions in the polymer chain [19]. The hydrothermal ageing of glass (or carbon) fiber/epoxy was shown to follow Fickian diffusion mechanism till saturation of the adhesive interface [20, 21]. Similarly, supported by atomistic simulations and experimental analysis, the diffusion coefficient of the water in a thermoset polymer was found to be decreasing with increasing epoxy density [22]. The reduction in the elastic modulus of the epoxy was attributed to the water-induced swelling, while the reduction of strain to fracture was attributed to water-ingression [22].

The observed interfacial degradation mechanisms under different exposures were found to be very sensitive to the examined adhesive/adherend material systems. For example, it was shown that the rubber-steel peel strength can be degraded by 50% with a trace level (less than 1µg/cm2) of plasticizer contaminant, whereas, it can be improved due to exposure to hydraulic oil [23]. Additionally, the adhesive bulk property degradation was very different when utilized in a bonded joint. For example, the strength of the bulk adhesive material has shown a modest reduction (~10%) with high levels of calcium grease contamination [24]. Whereas, the same adhesive material has shown a significant interfacial deterioration at a low
level of the same contamination [24]. Such observations highlight the complex interaction of the contamination on the mechanical properties of the adhesively bonded joints. It would affect the confined local plastic deformation of the adhesive, while concurrently greatly deteriorating the intrinsic interfacial adhesion of the adhesive-adherend pair.

Such dual interaction between the intrinsic interfacial adhesion and the local dissipation within the adhesive would affect the effective macroscopic bond line toughness. For example, increasing the testing temperature would drastically decrease the mode-I fracture toughness of the bond line [7]. This trend was attributed to adhesive strength reduction above the glass transition temperature, despite the increase in its ductility. Similarly, preexisting moisture in the CFRP composite substrates would lead to a reduction in glass transition temperature of the adhesive after the bonding process, accompanied by significant degradation in the bond line fracture toughness [12]. Aside from the service environment, it was also established in layered structure literature that limiting the role of plastic dissipation within the adhesive layer by reducing its thickness would have a marked effect on the macroscopically measured fracture toughness of the bond line [25-28].

This study explores the contamination-induced degradation mechanisms of bond line fracture toughness for a common adhesive/adherend system, exposed to different levels of a typical aerospace grade hydraulic fluid. A range of contaminant concentration was applied prior to the bonding process, in order to assess the residual bond line fracture toughness and the resulting fracture surface morphology. The macroscopic bond line fracture toughness was experimentally measured by double cantilever beam (DCB) test. Fracture surface analysis was performed on fracture surface morphologies to provide insight into the contamination-induced variation of bond line failure mode. In addition, the finite element method (FEM)
employing surface-based cohesive elements was utilized to extract the interfacial adhesion parameters. The combined experimental and numerical results were utilized to understand the degradation mechanisms induced by the bond line contamination.

**Material and Sample Preparation**

Five groups of DCB samples were fabricated to evaluate the mode-I bond line fracture toughness for varying contaminant concentrations. The fracture DCB samples consisted of two composite panels bonded to each other with an adhesive (Hysol EA9394) layer. The composite laminates, with a layup of $[\pm45^\circ, 0\,^\circ]_s$, were constructed by stacking 10 plies of Hexcel IM7-G/8552 unidirectional prepregs and two additional plies of Hexcel W3B-282 bi-directional weaved fabric at $\pm45^\circ$ on the top and bottom faces. Standard fabrication of vacuum bagging and hot-press curing methods were implemented. The adherend surfaces were treated by grit-blasting to enhance the average surface roughness to about $R_s \approx 5\mu m$, which is generally considered as a sufficient level of surface roughness for improved adhesion [29]. After the surface treatment process, the panel surfaces were cleaned by water and hexane, then the panels were left in a drying furnace at 160°F (71 °C) for 2h with heating and cooling rates of 5°F/min, following NAVAIR 01-1A-21 (see Sec. 6-7a (2)) technical manual [30].

This study utilizes four levels of hydraulic fluid contaminant (MIL-PRF-87257) concentrations: 1, 3, 10, 55 $\mu g/cm^2$, which correspond to non-volatile residue cleanliness levels of A, C, G, J, respectively [5]. The selected contaminant was first diluted by a volatile agent (e.g. Hexane) to the desired concentration. The diluted solution was uniformly applied
on the roughened and cleaned surface of one of the composite panel pair. The desired surface concentration level was achieved by controlling the dispensed volume of the solution. The resulting contamination level was verified by infrared spectroscopy to be within few percent. A 125μm thick Teflon film was used to create an initial crack starter at the edge of the samples with a nominal length of 50mm. In addition, the adhesive layer thickness was controlled by a 250μm thick shim that was inserted along the sample length, outside the gage width. The resulting bond line thickness was measured to be around \( t_{\text{adhesive}} = 400 \mu m \).

Subsequently, bonded composite panels were cured under 5psi (34.5kPa) pressure at room temperature (22 °C) for 16h. Finally, a rapid curing step was performed in a furnace at 190°F (88°C) for 2h. The resulting composite panels were cut into DCB samples with dimensions of 25.4 x 180 mm². Steel loading blocks were glued to the ends of the samples. Figure 3-1(a) shows the DCB sample configuration within the loading fixture and the utilized dimensions.

![Figure 3-1](image.png)

Figure 3-1  (a) Experimental loading configuration for the double cantilever beam test (b) Typical force-displacement curve, showing the initial loading-unloading step to sharpen the manufactured blunt notch, followed by the reloading step with a steady state interfacial crack propagation.
Experimental Procedure

The effective bond line fracture toughness was measured using DCB test method, according to ASTM-D5528-13 [31], a standard testing practice for mode-I interfacial fracture characterization of CFRP composites. All DCB tests were performed under displacement control using an Instron 8862 servo-electric computer controlled universal testing frame. A ramp displacement of $20 \mu m/s$ was applied. The applied cross-head displacement, force, and in-situ digital images of the interfacial crack growth were recorded simultaneously. Prior to all tests, initial loading and unloading steps were performed to sharpen the manufactured interfacial blunt crack-tip. The initial loading step was terminated right after a sudden force drop in force-displacement curve, which results in a crack growth of about 5-10 mm beyond the manufactured crack tip. The samples were then unloaded and the actual tests were performed with a sharpened interfacial crack tip. The slight variability of the initial crack length resulted in different loading stiffness for different samples. Figure 1(b) shows a representative set of force-displacement curves for the initial loading and unloading steps, as well as the steady state crack propagation. The interfacial crack growth was captured by a high-resolution digital camera (The SPOT™ Insight 4.0 Monochrome) with a 60mm micro lens (Nikon AF Micro Nikkor 60mm) at a 1 f/s frame rate. Approximately 400-500 sequential optical images with a resolution of $20 \mu m/pixel$ were captured for each DCB test. The instantaneous crack length was evaluated from the sequential images by utilizing an in-house developed digital image-processing tool in Matlab® to track the crack tip. The crack length measurement precision was estimated to be less than $10 \mu m$.

The mode-I strain energy release rate, $G$ was calculated using modified beam theory,
\[ G = \frac{\alpha_1}{\alpha_2} \frac{3P\delta}{2ba}, \]  

where \( P \) is the measured force, \( \delta \) is the applied cross-head displacement, \( \alpha \) is the instantaneous crack length, measured from the loading pin center to the current crack tip position, and \( b \) is the sample width, as indicated on Figure 3-1(a). The coefficient, \( \alpha_1 \), is a nondimensional correction factor for large displacement effect,

\[ \alpha_1 = 1 - \frac{3}{10} \left( \frac{\delta}{a} \right)^2 - \frac{3}{2} \left( \frac{\delta t}{a^2} \right). \]  

The coefficient, \( \alpha_2 \), is another dimensionless correction factor accounting for the effect of the end loading blocks on the effective sample stiffness,

\[ \alpha_2 = 1 - \left( \frac{\tilde{L}}{a} \right)^3 - \frac{9}{8} \left[ 1 - \left( \frac{\tilde{L}}{a} \right)^2 \right] \left( \frac{\delta t}{a^2} \right) - \frac{9}{35} \left( \frac{\delta}{a} \right)^2. \]  

Here \( t \) is the distance from the loading pin center to the center line of the upper composite panel, and \( \tilde{L} \) is the half length of the end block [32]. These coefficients were found to be of order unity and would affect the estimate of \( G \) within 5-10%.

**Numerical Modeling Approach**

The modeling approach employs the large-scale bridging model proposed by Tvergaard and Hutchinson [33], wherein plasticity plays an important role in the macroscopic toughness of polymer-based adhesive joints. The bond line thickness was shown experimentally to affect the macroscopic bond line toughness [25-28]. The contribution of plastic deformation of the adhesive layer in the effective toughness controls the observed
thickness-toughness dependence. Thus, the macroscopic bond line toughness, $G_{eff}$, can be considered as the confluence of the cohesive (interfacial) fracture toughness $G_0$ and the energy dissipation through plastic (or inelastic) deformation, $W_p$, such that

$$G_{eff} = G_0 + W_p$$

(4)

It was shown that $W_p$ can dominate $G_{eff}$ with the existence of inelastic deformation of the adhesive layer, even for mode-I interfacial fracture [34, 35]. In the case of brittle interfacial fracture, however, $W_p$ can amount to an insignificant value. The implemented numerical model incorporates both types of energy dissipation mechanisms during the interfacial fracture process, the intrinsic interfacial adhesion and the plastic dissipation within the adhesive layer. The former was simulated by surface-based cohesive elements, while the elasto-plastic continuum elements were used to model plasticity of the adhesive layer and the resulting plastic energy dissipation. The numerical simulations were primarily utilized to characterize the cohesive fracture toughness and work of plasticity individually.

Numerical simulations were performed using the commercial FEM package SIMULIA Abaqus 6.14-2. DCB sample geometry was modeled using 2-D 4-node quadrilateral linear plane strain elements (CPE4). Figure 3-2(a) shows the finite element model geometry, mesh and boundary conditions. A single layer of surface-based cohesive elements were introduced at one of the adhesive/adherend interfaces to simulate interfacial crack propagation, whereas the other interface was tied together. A bilinear traction-separation law [36] was employed to model the interfacial adhesion as shown in Figure 3-2(b). The utilized cohesive zone model did not account for fracture mode-mixity, as the DCB test was shown to be only sensitive to mode-I cohesive parameters [37]. The mesh was
refined in front of the crack tip along the cohesive interface. The refined mesh size was selected to be $10 \mu m$ so that there are at least 5 elements within the cohesive length for all contamination levels [38]. The cohesive zone length was estimated by Hillerborg’s model [39]. It was also confirmed that the numerical solution is independent of the mesh size. The adhesive layer was modeled to be $400 \mu m$ thick, with uniform square elements. The details of cohesive surface implementations and the numerical model can be found in Refs. [40-42].

Since the DCB configuration is dominated by the opening displacement, which arise from the flexural bending of the adherend panel, the adherend composite panels were effectively modeled as an isotropic elastic material. Knowing the transverse property exactly

Figure 3-2 (a) Finite element model geometry, mesh and boundary conditions. (b) The utilized bilinear traction-separation law, showing self-similar scaling approach to model degradation.
of the adherend composite panel will have no effect on the interfacial fracture. Additionally, the adherend panel has a ±45 fabric, with quasi-isotropic response, thus having an effective isotropic response would be sufficient to assess the interfacial fracture toughness under mode-I loading. The adhesive layer was modeled as an isotropic elastic-plastic material. The effective flexural stiffness of the adherend panels was obtained from flexural bending tests with a four-point loading configuration according to ASTM-D7264/D7264M-07 [43], and was estimated to be \( E = 64 \text{GPa}, \nu = 0.3 \). The mechanical properties of the adhesive were \( E = 4.3 \text{GPa}, \sigma_y = 69 \text{MPa}, \nu = 0.43 \) [44], with a modest hardening exponent of \( n = 1/N \approx 6.2 \) according to the Ramberg-Osgood model [45]. The hardening exponent was evaluated by the ratio, work/complementary work for the range of interest (up to 3.5% strain) of the stress-strain curve of the adhesive material, reported by Guess et al. [44].

**Experimental Results**

**Effective Bond Line Fracture Toughness**

Four DCB samples were tested for each level of contaminant concentration. Figure 3-3 summarizes the force-displacement curves for all the tested cases (control, contamination levels C, G and J) and the corresponding estimated energy release rates, \( G \)-curves. In each case, the slight variation in the initial loading stiffness arises from the differences in the initial crack length, \( a_0 \), which was determined after the initial loading/unloading sharpening cycle; required by the ASTM standard. The bond line strength shows a gradual reduction with increasing contaminant concentration. Both the initiation and steady state level of the energy release rate exhibit a progressive drop with increasing contaminant concentration. The
critical energy release rate at initiation for the control samples is about $G \approx 400 \ J/m^2$ and gradually reaches a steady state average value of $G \approx 700 \ J/m^2$ as shown in Figure 3-3(e). Similarly, for the level C contaminated samples, the average initiation fracture energy is recorded to be about $G \approx 300 \ J/m^2$, while the steady-state average level is about $G \approx 450 \ J/m^2$ (Figure 3-3(f)). However, there is not a considerable difference between the average initiation and propagation energy levels for the contaminated cases as shown in Figures 3-3(g, h). A key observation is the role of a trace level of the examined contaminant (level C; 3 µg/cm², Figures 3-3(b, f)), which reduces the average bond line strength by about 15%, and the average interfacial fracture toughness by about 30% compared to the uncontaminated case, Figures 3-3(a, e).

For comparison, the steady state level of the strain energy release rate is considered as the macroscopic (or effective) bond line toughness, $G_{eff}$. A summary of the measured $G_{eff}$ values are presented on Figure 3-4(a), as a function of the contaminant concentration on a logarithmic scale. The control case is represented by contaminant concentration 0.01 µg/cm² in order to present all cases on a logarithmic scale. The measured $G_{eff}$ is progressively reduced with the increase in contaminant concentration level. Though level A contamination does not induce a noticeable effect on $G_{eff}$, comparing to the baseline value. Level A is typically considered to be a clean surface according to MIL-STD-1246C [5]. However, levels C and G result in significant deterioration up to a 50% reduction of $G_{eff}$. Level J exhibits severe degradation of $G_{eff}$ to less than 10% of the reference value.
Figure 3.3 Summary of the experimental results) for the examined cases, showing the DCB force-displacement curves and the derived fracture energy release rate, G.
Figure 3-4(a) exhibits a clear correlation between the measured $G_{eff}$ and the contaminant concentration $\overline{C}$. The interfacial surface adhesion can be correlated with the interfacial contamination concentration [42], through an Arrhenius-type relation of modified Gibbs adsorption equation [46]. Here we explored a similar correlation of the form:

$$\frac{G_{eff}}{G^*_{eff}} = 1 - \lambda \ln \left( 1 + \xi \frac{C}{C^*} \right)$$

and

$$\lambda = \frac{1}{\ln(1 + \xi)}.$$  \hspace{1cm} (5)

Where $G^*_{eff}$ is a reference level for the effective toughness of the uncontaminated interface and is taken to be $G^*_{eff} = 670$, and $\overline{C}^*$ is a saturation concentration of the contaminant at which the interfacial adhesion greatly deteriorated ($G_{eff}/G^*_{eff} \to 0$). By extrapolation of the experimental data, the saturation concentration was estimated to be $\overline{C}^* = 100 \mu g/cm^2$. $\xi$ is the correlation fitting parameter, and is found to be $\xi = 73.4$. $\lambda$ sets the correlation lower bound for $G_{eff}/G^*_{eff} \to 0$ when $\overline{C} \to \overline{C}^*$, therefore, is related to $\xi$ and is found to be $\lambda = 0.232$. Physically, $\lambda$ is proportional to the slope of $G_{eff} - \ln(C/\overline{C}^*)$, which was also considered as a constraint on $\lambda$ during the least square fitting of the correlation. It should be noted that the domain of validity of Eq. (5) is limited to the examined domain of $\overline{C}/\overline{C}^* = \{0,1\}$. This correlation has the potential to provide estimates of the residual bond line toughness in adhesively bonded structures for a known contamination level. However, it should be noted that the present correlation is valid only for the examined adhesive/adherend material system, as well as, the applied contaminant type.
Figure 3-4  (a) Summary of effective fracture toughness measurements for the examined cases as a function of contamination concentration, highlighting the severe chemical degradation of the bond line toughness. (b) The observed correlation between the normalized effective fracture toughness and the contaminant concentration.
Role of Contamination on Interfacial Crack Growth and Morphology

The observed gradual decrease of the interfacial strength and toughness can be linked with the change of the interfacial failure modes and fracture surface morphologies. The force-cross head displacement highlights several aspects of the failure mechanisms. Figure 3-4 shows the measured force and crack length curves as a function of the applied cross head displacement for the control and level J contaminated samples. The control case, Figure 3-5(a), exhibits a minor nonlinearity near the force plateau on the force-displacement curve, right before the start of the crack growth. This is manifestation of the growth of plastic process zone within the adhesive layer and the corresponding large scale bridging. After attaining the critical interfacial strength, the control case presents an intermittent force-displacement curve with abrupt force drops. The corresponding interfacial crack propagation shows multiple intermittent growth and arrest events, coinciding with the load drops. Such unsteady crack propagation could be associated with the collapse and reestablishment of the plastic process zone within the bond line. The optical image insert in Figure 3-5(a) for the morphology of the propagating crack shows a wavy path, providing clear evidence of the intermittent crack growth behavior. The crack typically kinked into the adherend material, resulting in a ductile “fiber-tear type” failure mode. No crack kinking into the adhesive and crossing to the other interface was observed. To the contrary, Figure 3-5(b) shows the absence of nonlinearities within the initial part of the loading curve up to the onset of crack propagation for the contaminated case (Level J). This is an indication of the absence of plastic deformation within the adhesive layer. The diminishing of the plastic process zone resulted in a more stable crack propagation with linear growth, as shown in Figure 3-5(b).
Figure 3-5  The measured force and crack length as a function of the applied displacement, showing the distinct changes in the failure modes. (a) Control case showing ductile fiber-tear type failure. (b) Contaminated case showing brittle adhesive-type failure.
The optical image insert in Figure 3-5(b) shows a smooth crack path, which is attributed to a brittle “adhesive type” failure mode [47] as a result of the contamination-induced degradation of the interfacial strength and toughness.

Figure 3-6 Optical and SEM images of the fracture surfaces. (a, b) Control case exhibiting rough fracture surface with hackle marks, associated with fiber-tear-type failure mode. (c, d) Level J contamination case showing a thin adhesive layer covering the fibers, consistent with adhesive-type failure mode.

The observed changes of the failure mode can be further revealed through the composite optical and scanning electron microscope (SEM) images of Figure 3-6 for the
fracture surfaces. In the control case, the fabric weaves (~1.5mm) are clearly visible in Figures 3-6(a, b), indicating the roughened fracture surface. The inserts in Figure 3-6(b) show a large magnification of the “hackle-like” surface features on the fibers and the plastic deformation and failure of the adherend matrix. The prevailed failure mode is fiber-tear type, which clearly indicates a strong interfacial strength and the resulting enhanced ductility of the adhesive layer. However, the level J contaminated surface displays a very smooth adhesive surface, Figures 3-6(c, d). After further examination of the marked spots in Figure 3-6(c) using a noncontact surface profilometer, a low-amplitude large-wavelength modulation was observed; dictated by the weave periodicity. The higher SEM magnification of Figure 3-6(d) of the fracture surface morphology suggests that the separation occurs at the adhesive/adherend interface, with a thin layer of adhesive remaining on the adherend panel. These characteristics are commensurate of a brittle “adhesive type” failure mode, resulting from the degraded interfacial strength, and absence of plastic dissipation within the adhesive layer or the adherend matrix.

**Numerical Results and Discussions**

**Calibration of Cohesive Zone Parameters**

The two parameters $G_0$ and $\hat{\sigma}$ of the bilinear traction-separation law were calibrated by matching the peak force of the experimentally measured force-displacement curve for each contamination level [35]. Then, $G_0$ was varied by scaling the linear softening domain while keeping its slope constant so that the traction-separation law remains self-similar as shown in Fig. 2(b). Such variability facilitates the scalability between interfacial fracture
toughness and interfacial cohesive strength, such that $G_0 \sim \hat{\sigma}^2$. Keeping the self similarity of the traction-separation law resulted in a reasonable representation of the experimentally measured maximum fracture force for the DCB configuration for all the examined cases. The resulting energy release rate, calculated on a contour enclosing a stationary crack tip, was compared to the effective fracture toughness, $G_{\text{eff}}$ evaluated from the experiment (Fig. 4(a)) for all examined cases. The typical discrepancies between the predicted and measured values of $G_{\text{eff}}$ were within a few percent. Table 3.1 summarizes the calibrated cohesive zone parameters for the examined concentration levels.

Table 3.1 The numerically calibrated interfacial fracture parameters for the examined contamination concentrations. (* Average values with standard deviation).

<table>
<thead>
<tr>
<th>$\bar{C}$ ($\mu g/cm^2$)</th>
<th>$\hat{\sigma}$ (MPa)*</th>
<th>$G_0$ ($J/m^2$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>128.0±6.0</td>
<td>228.4±21.4</td>
</tr>
<tr>
<td>1</td>
<td>128.0±6.0</td>
<td>231.7±7.2</td>
</tr>
<tr>
<td>3</td>
<td>105.0±7.0</td>
<td>153.9±20.5</td>
</tr>
<tr>
<td>10</td>
<td>99.5±2.5</td>
<td>137.4±7.0</td>
</tr>
<tr>
<td>55</td>
<td>59.5±3.5</td>
<td>49.7±5.8</td>
</tr>
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</table>

Figure 3-7 shows the numerically obtained force-displacement and $G$-curves (dashed red lines), respectively, superimposed on a set of experimental measurements for all the examined cases. Qualitatively, the numerical simulations were able to reasonably reproduce the experimentally measured trends in terms of matching maximum failure load and $G_{\text{eff}}$ values. However, the numerical predictions do not demonstrate the intermittent growth and arrest of the interfacial crack. To capture such physical behavior, the analysis must account for the inertial effects as well as the stochastic defect distribution, which are beyond the scope of the current study.
Figure 3-7  (a) A representative set of force-displacement curves and (b) the corresponding fracture energy release rate G-curves, obtained from DCB experiments, along with the numerical results (dashed lines), for the examined cases.

**Contamination-induced Limitation of Plastic Energy Dissipation in Bond Line**

The combined experimental and numerical results provide a mechanistic insight into the complex role of the contamination on the bond line toughness. Such compound effect of the contamination on $G_0$ and $G_{\text{eff}}$ can be summarized in Figure 3-8, presenting an experimentally measured and numerically calibrated map. Here, $G_0$ and $\sigma^*$ are the numerically calibrated values for each level of contaminant concentration, and correspond to the experimentally measured $G_{\text{eff}}$. The difference between $G_{\text{eff}}$ and $G_0$ represents the energy dissipation through plastic deformation, $W_p$ within the adhesive layer. Progressively increasing the concentration deteriorates both $\sigma^*$ and $G_0$, with $G_0$ dropping four-fold from its reference value for level J contamination. At such a level, $G_{\text{eff}}$ approaches $G_0$ with almost full absence of the plastic dissipation within the adhesive layer.
Figure 3-8 The experimentally measured and numerically calibrated variation of the effective interface toughness $G_{\text{eff}}$ (circles) and the intrinsic fracture toughness $G_0$ (squares) as a function of the cohesive strength $\sigma$, highlighting the role of the contamination level.

The observed contamination-induced degradation of $\sigma$ can be visualized in Figure 3-9, which illustrates the opening stress ($\sigma_{22}$) contours in the vicinity of interfacial crack for the control and level J contamination cases. Level J contamination reduces the interfacial critical strength $\sigma$, and thereby considerably limits the extent of fracture process zone (red-colored region in front of the crack tip) within the adhesive layer. In the control case, the process zone size is of the same order as the adhesive layer thickness. It is significantly diminished in case of the level J contamination.
Figure 3-9 The opening stress ($\sigma_{22}$) contours in the vicinity of interfacial crack for the control and level J contamination cases, highlighting the constraint effect of level J contamination on the extent of plastic process zone size in front of the interfacial crack tip within the adhesive layer.

The observed limitation of the plasticity can be further clarified in Figure 3-10, by considering how the plastic zone size varies with the changes in the cohesive to yield strength ratio ($\hat{\sigma}/\sigma_y$) for the adhesive. The plastic zone size, $R_0$ is estimated from the numerical simulations at a threshold effective plastic strain of 1%, as shown in the insert images in Figure 3-10. When $\hat{\sigma} > \sigma_y$ for the reference case, the plastic process zone within the adhesive layer can extend to about 35% of the bond line thickness. As the contaminant concentration increases, $\hat{\sigma}$ significantly deteriorates below $\sigma_y$ and the plastic zone size diminishes to less than 4% of the bond line thickness. The observed diminishing of $R_0$ with increasing contamination level can be further visualized through the insert images in Figure 3-10, which shows the effective plastic strain contours within the adhesive layer for the
control and level C contaminated cases. As can be clearly seen, the extent of wake of plasticity behind the interfacial crack tip is reduced for the level C contamination compared to the control case. It is evident that when $\hat{\sigma}$ falls below the tensile strength of the adhesive layer, $\sigma_y$, the interface starts to separate before the interface reaches the limit of its plastic flow. More importantly, a trace level of the examined contamination (level C, 3 µg/cm$^2$), has a marked effect on the process zone size with about a 25% reduction. This effect is manifested as 30% reduction in the macroscopic interface toughness. Note that the plastic process zone size scales with $G_c/\sigma_y^2$ [33, 40].

Figure 3-10 Summary of the numerical estimates of bond line process zone size as a function of cohesive strength to yield strength ratio. The insert depicts the effective plastic strain contours within the adhesive layer showing the wake of plasticity behind the interfacial crack for the control and level C contaminated cases, highlighting the limited plastic dissipation with level C contamination.
From the observed trends, it can be concluded that the role of the contamination in reducing the intrinsic surface adhesion is accompanied with further shielding of the plastic energy dissipation within the bond layer. This compound effect significantly deteriorates the effective macroscopic bond line toughness, $G_{\text{eff}}$.

**Conclusion**

The present study provided an insight into the contamination-induced degradation of bond line toughness for an aerospace grade hydraulic fluid contaminant with relevant concentration levels. The experimentally measured macroscopic bond line toughness and strength exhibited a progressive drop with increasing contaminant concentration. It was found that a trace level (level C; 3 µg/cm$^2$) of the examined contaminant may result in about 15% reduction in the bond line strength and 30% in the macroscopic bond line toughness, compared to their reference levels. The fracture surface topology analyses revealed ductile-to-brittle transition with an increase in contamination level. The transition is attributed to the absence of plasticity of the adhesive layer due to contamination. Finite element analysis showed the dual role of the contamination in reducing the intrinsic adhesion strength of the interface as well as reducing or completely shielding the plastic dissipation within the adhesive layer. At high concentration levels, the macroscopic toughness reaches the level of intrinsic adhesion toughness with nearly full absence of plastic dissipation. Additionally, an Arrhenius-type correlation scaling was observed between the normalized macroscopic toughness and the contaminant concentration, which might facilitate non-destructive
inspections of bond line integrity. The presented framework lays the foundation for understanding the role of the contaminant concentration on the bond line integrity for adhesively bonded composite structures.

References


45. Ramberg W, Osgood WR. Description of stress-strain curves by three parameters, 1943.


CHAPTER 4. PREDICTION OF INTERFACIAL SURFACE ENERGY AND EFFECTIVE FRACTURE ENERGY FROM CONTAMINANT CONCENTRATION IN POLYMER-BASED INTERFACES

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Denizhan Yavas, Ashraf F. Bastawros
Department of Aerospace Engineering, Iowa State University, Ames, IA 50011-2271

Abstract

The principals of interfacial fracture mechanics and modified Gibbs adsorption equation are utilized to provide a predictive correlation for the macroscopic (effective) fracture toughness of polymer-based adhesive interfaces, exposed to varying level of contaminant concentration. The macroscopic fracture toughness measurement by double cantilever beam test exhibits a progressive deterioration with the increase of the contaminant surface concentration. The associated variation of fracture surface morphology exhibits ductile-to-brittle failure transition, caused by the contamination-induced suppression of plastic deformation within the adhesive layer. The corresponding intrinsic interfacial surface energy is extracted by finite element simulation, employing surface-based cohesive elements. The modified Gibbs adsorption equation is utilized to correlate the contamination-induced degradation of the interfacial surface energy as a function of contaminant surface
concentration. Interfacial fracture mechanics principals are applied to extend the correlation to the macroscopic fracture toughness of the interface.

**Introduction**

Polymer-based adhesive joints have been extensively utilized in a wide range of industrial applications, with the advantages of high strength-to-weight ratio, uniform stress along the bond line, and design flexibility for assembly of complex structures [1]. Aerospace industry has pioneered the adhesion technology, especially with utilization of carbon fiber reinforced polymer (CFRP) composites in airframe structures. However, one of the major concerns with polymer-based adhesive joints is the surface contamination under severe operating conditions, which affects performance and long-term reliability of bonded structures [1,2]. The deterioration of fracture toughness cannot be assessed without a destructive interfacial fracture experiment, such as double cantilever beam test (DCB), among many others. The structural reliability of polymer-based adhesive joints has been broadly studied under different environmental conditions, including service temperature [3-5], moisture [6-10], chemical contaminants [11-14], and radiation [15]. These studies have shown that degradation mechanism is extremely sensitive to the adhesive/adherend material system, as well as the source of surface contamination, which also strongly controls the resulting failure mode. For example, Davis [16] has shown that the rubber-steel peel strength can be degraded by 50% with a trace level (less than 1µg/cm²) of plasticizer contamination. Accordingly, a proper characterization of the contamination-adhesion interaction in polymer-based adhesive joints requires a destructive evaluation of a well-defined contaminant-adhesive system with controlled level of surface concentration.
This work is a naive attempt to correlate the contamination-induced degradation of macroscopic fracture toughness, $G_o$, with the contaminant surface concentration, $C_{HF}$, which could be measured non-destructively by spectroscopic methods [17]. A common adhesive/adherend system (Hysol EA9394/Hexcel IM7-G/8552) exposed to a typical environmental chemical (aviation hydraulic fluid, MIL-PRF-87257) is systemically examined. $G_o$ is experimentally measured by DCB test. Interfacial surface energy, $\gamma$ is evaluated numerically from finite element modeling (FEM) employing cohesive-based surfaces. The modified Gibbs adsorption equation is utilized to correlate the contamination-induced degradation of $\gamma$ over two decades of $C_{HF}$ variation. Principals of interfacial fracture mechanics using the large-scale bridging model proposed by Tvergaard and Hutchinson [18], are utilized to provide the corresponding predictive correlation for $G_o$, which considers the large contribution of plastic deformation of the polymer-based interface to the effective work of fracture.

**Experimental and Modeling Framework**

The experimental DCB fracture samples consist of two composite panels bonded to each other by an adhesive layer with thickness $h = 400\mu m$. The current study utilizes four levels of contamination surface concentration: $C_{HF} = 1, 3, 10, 55 \mu g/cm^2$, which correspond to non-volatile residue cleanliness levels of A, C, G, J, respectively, defined in MIL-STD-1246C [19]. The surface contaminant concentration was accomplished by Hexane dilution to the desired level. The diluted solution was evenly applied on the roughened and cleaned
surface of the adherend panels. The desired surface concentration was controlled by the height of the solution, and verified by performing infra-red spectroscopy to be within few percent. Three DCB fracture samples were tested for each level of contamination.

All DCB tests were performed under displacement control at a loading rate of 0.02 mm/s using an Instron 8862 servo-electric computer controlled testing frame, following ASTM-D5528-13 [20]. Force, cross-head displacement and in-situ digital images of the interfacial crack growth were recorded simultaneously. Prior to all tests, an initial loading/unloading step was performed to sharpen the manufactured blunt crack-tip. Mode-I energy release rate, $G$ was calculated from the measured force, cross-head displacement, and instantaneous crack length using modified beam theory [20]. Thereby, $G_o$ corresponds to the steady state levels of the $G$-curves.

Table 4.1 The numerically calibrated interfacial fracture parameters for the examined cases (* Average values presented with the corresponding standard deviation).

<table>
<thead>
<tr>
<th>$C_{HF}$ (µg/cm²)</th>
<th>$\hat{\sigma}$ (MPa)*</th>
<th>$\gamma$ (J/m²)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>128.0±6.0</td>
<td>228.4±21.4</td>
</tr>
<tr>
<td>1</td>
<td>128.0±6.0</td>
<td>231.7±7.2</td>
</tr>
<tr>
<td>3</td>
<td>105.0±7.0</td>
<td>153.9±20.5</td>
</tr>
<tr>
<td>10</td>
<td>99.5±2.5</td>
<td>137.4±7.0</td>
</tr>
<tr>
<td>55</td>
<td>59.5±3.5</td>
<td>49.7±5.8</td>
</tr>
</tbody>
</table>

Modeling to estimate $\gamma$ was performed by the commercial FEM package SIMULIA Abaqus 6.14-1, employing cohesive surfaces and elastic-plastic continuum elements to model the adhesive layer. $\gamma$ was estimated from the simulations by iteratively changing the critical cohesive traction, $\hat{\sigma}$, to match the peak force of the experimentally measured force-displacement curves with the corresponding estimate from the model, for each $C_{HF}$ case.
The resulting macroscopic energy release rate, calculated on a contour enclosing the crack tip, was compared to the experimentally measured $G_o$, with typical discrepancies within few percent. Table 4.1 summarizes the utilized interfacial fracture parameters for the examined contamination levels. Elaborate details of sample preparation, experimental details and the geometric modeling can be found elsewhere [21].

**Results**

A representative set of force-displacement curves for the examined contamination cases are shown in Figure 4-1(a), along with the simulation results (dashed lines). The slight variation in the initial loading stiffness arises from the differences in the initial crack length, being determined after an initial loading/unloading cycle to sharpen the crack tip. The control case has shown a minor force plateau on the force-displacement curve before the start of the crack growth. To the contrary, all contamination levels have shown a linear increase up to the onset of crack growth, which can be attributed to the contamination-induced suppression of plasticity within the bond line. As can clearly be seen, the bond line strength exhibits a gradual reduction with increasing the surface contamination concentration. It should be noted that even a trace level of contamination (level C, 3 µg/cm$^2$) can result in a significant reduction of the bond line strength, in excess of 30-35%, compared to the control case. Upon reaching the critical load carrying capacity of the bond line, the measured force has exhibited progressive drops, accompanied with successive crack propagation. The associated zig-zag pattern is attributed to the intermittent propagation and arrest of the interfacial crack or relaxation of the fracture energy, followed by building up of the fracture driving forces. The
corresponding $G$-curves, along with the FEM results (dashed lines), are presented in Figure 4-1(b). Qualitatively, the numerical simulations reproduced the experimentally measured trends in terms of matching maximum failure load and the steady-state energy release rate values. Sudden jumps in the measured energy release rate of the control case clearly show the arrest and propagation of the crack, which is attributed to the reestablishment and collapse of the plastic process zone within the bond line. To the contrary, crack growth along the contaminated surface is relatively stable. In fact, the stability of the crack growth tends to increase for increasing contamination level, which can be perceived as another evidence for the contamination-induced shielding of the plastic process zone within the adhesive layer.

Figure 4-1 (a) A representative set of force-displacement curves and (b) the corresponding fracture energy release rate $G$-curves, obtained from DCB experiments, along with the numerical results (dashed lines), for the examined cases.

Figure 4-2 shows optical images of the fracture surfaces for the control case, as well as 3 and 55 µg/cm$^2$ contaminated cases, respectively. The fabric weave periodicity is about 1.5mm. In the control case (Figure 4-2(a)), the fabric weave periodicity completely appeared
on the fracture surface. This is a clear indication of fiber-tear failure, which is generally associated with enhanced ductility of the adhesive layer. To the contrary, the 55 µg/cm² contaminated fracture surface displays smooth adhesive surface, Figure 4-2(c) with large wavelength modulation dictated by the weave periodicity. The separation occurs at the adhesive/adherend interface, which is attributed to brittle interfacial (adhesive) failure [22]. The intermediate contamination level of 3 µg/cm² case exhibits a combination of both failure modes, Figure 4-2(b).

Figure 4-2 Optical images of the fracture surfaces of (a) the control, (b) 3 µg/cm², and (c) 55 µg/cm² contaminated cases, showing the marked difference in roughness.

The corresponding topologies of fracture surface are imaged by 3-D non-contact surface profiler (Zygo NewView™ 6300), and shown on Figure 4-3. The selected field of view (1.45x1.05 mm²) over the fracture surface is large enough to capture the interfacial fracture process zone and show the details of the interfacial plastic deformation. Typically, the adhesive layer thickness represents the relevant length scale for the interfacial adhesion process. For common polymer matrix composite systems and adhesives, the interfacial fracture processes zone is smaller than the film thickness. The average surface roughness (}
$R_a$) were measured to be $R_a \approx 11, 7.4, 4.7 \mu m$ respectively for the three presented cases on Figure 4-2.

![Figure 4-3](image)

Figure 4-3  Topologies of the fracture surface, measured by 3D non-contact surface profilometer with 1.45x1.05 mm$^2$ field of view. (a, b) 3D rendering of the fracture surface topologies. (c, d) Height profiles along the marked lines, showing the roughening and extent of plasticity in the control case, and the smooth profile in the 55 µg/cm$^2$ contaminated case.

The corresponding height profiles on the lines indicated in Figure 4-3(a) and 4-3(b) are also shown on Figures 4-3(c) and 4-3(d), and clearly reveal the contamination-induced suppression of plastic deformation and reduced roughness of the fracture surface profile. It should be noted that the persistent wavelength on the interfacial fracture surface topology, which could be interpreted as the process zone size, is much smaller than the weave periodicity. It is about 250-400 µm for the control case, and around 100µm for the 55 µg/cm$^2$
contaminated case. Based on these observations, one can notice a ductile-to-brittle failure mode transition, accompanied with a decrease in the geometric roughness of the fracture surface and the corresponding fracture process zone size. Such failure mode transition can be perceived as another evidence of the suppression of plastic deformation of the adhesive layer due to contamination.

Figure 4-4  Summary of the experimentally measured macroscopic fracture energy (solid squares) and the numerically calibrated interfacial surface energy (open squares) as a function of contamination concentration. The error bars depict standard deviation of the data. The dashed and dotted lines stand for the corresponding predictive correlations of Eqs. (3) and (6).
Summary of the experimentally measured $G_o$ (solid squares) and the numerically estimated $\gamma$ (open squares) are shown in Figure 4-4 as a function of the contaminant surface concentration, $C_{HF}$. The DCB fracture tests showed that $G_o$ is gradually deteriorated with the increase in $C_{HF}$, while suppressing plastic deformation within the adhesive layer. For the reference case, $G_o$ is about 3-4 times $\gamma$.

**Predictive Correlation Laws**

The difference between the intrinsic interfacial adhesion and the macroscopically measured toughness is amplified by the plastic (or inelastic) dissipation within the adhesive layer [23, 24]. Thus, $G_o$ can be written as the confluence of $\gamma$ and the energy dissipation through plastic (or inelastic) deformation, $W_p$, such that [18];

$$G_o = \gamma + W_p.$$ (1)

However, increasing $C_{HF}$ leads to a progressive drop in $\gamma$, which results in plasticity shielding within the interface layer and limits $W_p$. At the limit, when $C_{HF} \geq C_{cr}$, where $C_{cr}$ is a critical contaminant concentration, $G_o$ reaches $\gamma$ and the plastic dissipation within the adhesive layer is completely shielded ($W_p \rightarrow 0$). By extrapolating the trends for the measured $G_o$ and the simulation-based estimated $\gamma$ on Figure 4.4, the critical concentration was found to be $C_{cr} \approx 100 \mu g/cm^2$. 
The suggested scaling of $\gamma$ and $G_o$, with $C_{HF}$ could be addressed by invoking the modified Gibbs adsorption isotherm equation [25, 26] and utilizing the equivalence between surface energy and surface tension,

$$\gamma = \gamma_o - RT \Gamma_i \ln(1 + K_i a_i).$$

(2)

Here, $\gamma_o$ is the surface energy of the pristine interface without any surface contamination ($\gamma|_{C_{HF}=0} = \gamma_o$). For the examined adhesive/adherend material system,

$$\gamma_o \approx 228 \text{ J/m}^2,$$

which is the average surface energy of the control case. $R$ is the universal gas constant ($R = 8.3145 \text{ J/K mol}$). $T$ is the temperature ($T = 295 K$, room temperature).

$\Gamma_i$ is the saturated surface excess concentration of the surface-active contaminant $i$, adsorbed per unit area. $K_i$ is the adsorption coefficient of component $i$, and $a_i$ is the activity of species $i$ on the surface, and is proportional to the mass percent concentration, $C_i$. In the current experiment, $C_{HF}$ is the contaminant mass per unit surface area. A reference state of the concentration, $C = C_{cr}$ is utilized for normalization purpose, to facilitate the utilization of Eq. (2). The proposed modified form will be,

$$\gamma = \gamma_o - RT \Gamma_{HF} \ln\left(1 + A\tilde{C}_{HF}\right), \quad \text{and} \quad \tilde{C}_{HF} = C_{HF} / \tilde{C}$$

(3)

where $\Gamma_{HF}$ is the slope of $\gamma - \ln\left(\tilde{C}_{HF}\right)$ curve. For the examined adhesive/adherend materials and the applied contaminant, $\Gamma_{HF} \approx 1.73 \times 10^{-2} \text{ mol/m}^2$. $A$ is the proportionality constant and can be determined by least square fitting of the numerically evaluated $\gamma$. The proportionality constant was found to be $A \approx 100$, which seems to depend on the choice of the reference state, $\tilde{C}$ used in the normalization of the contaminant concentration. A different choice of
$\bar{C} \approx 1 \mu g/cm^2$ might be more feasible as it would represent the trace level of the contamination, wherein no degradation in the macroscopic adhesion strength would commence. However, such choice would render $\bar{C}_{HF} > 1$, which might represent an inconsistent definition of the normalized concentration. Accordingly, the prediction of Equation (3) is plotted on Figure 4-4 (dashed line) for the numerically estimated $\gamma$. It exhibits a good match for the range of $\gamma$, in terms of predicting the degradation of interfacial surface energy for the two decades range of the examined surface contaminant concentration.

The macroscopic fracture energy $G_o$ can also be correlated to the level of normalized surface contaminant concentration $\bar{C}_{HF}$ through Equations (1) and (3). Though, the level of plastic dissipation has to be estimated. A measure of $W_p$ (dissipated energy per unit area of the interface) can be estimated from the strain energy density (scales with $\sigma_y \dot{\varepsilon} = n \sigma_y \dot{\sigma}/E$; where $\sigma_y$ is the yield strength, $E$ is the Young’s modulus, and $n$ is the hardening exponent of the adhesive, and $\dot{\sigma}$ is the cohesive strength which scales with $\gamma$; $\gamma = \dot{\sigma} \ell/2$ for the same cohesive length, $\ell$) and the size of the process zone (scales with $R_0$). Tvergaard and Hutchinson [18] considered $R_0$ to be approximately associated with the plastic zone size as long as $R_0 < h$, and $G_o > \gamma$. When plasticity has negligible contribution, the crack propagates at the interface, at a constant applied stress intensity factor. $R_0$ is defined as a reference length scale,

$$R_0 = \frac{1}{3\pi} \left( \frac{K_0}{\sigma_y} \right)^2 = \frac{1}{3\pi(1-v^2)} \frac{E \gamma}{\sigma_y^2}. \quad (4)$$
Hence the plastic dissipation per unit area of the interfacial surface created can be estimated as,

\[ W_p \sim \frac{n\sigma_y \gamma}{E\ell} R_0 \sim \frac{n\gamma^2}{\sigma_y \ell}. \]  \hspace{1cm} (5)

The presented scaling in Eq. (5) suggests a strong influence of the adhesive mechanical properties, \( n \) and \( \sigma_y \) on \( W_p \). The authors have previously shown that the examined contaminant does not exhibit a noticeable effect on \( E \) and \( \sigma_y \) of the examined adhesive [21]. Accordingly, the combined Eqs. (1) and (5) suggest that, while not intuitively, \( G_o \) can be expressed as a quadratic function of interfacial surface energy, \( \gamma \), such that;

\[ G_o \approx \gamma + \frac{2\lambda n}{3\pi(1-\nu^2)} \left( \frac{1}{\ell \sigma_y} \right) \gamma^2. \]  \hspace{1cm} (6)

Here \( \lambda \) is a geometric fitting parameter of order unity. Using least square fit of the macroscopic \( G_o \), it is found to be \( \lambda \approx 1.63 \), and for the adhesive mechanical properties of \( E = 4.3 \text{GPa}, \sigma_y = 69 \text{MPa}, \nu = 0.37, n = 6.2 \) [27]. Accordingly, one can utilize Equation (6) in conjunction with Equation (3) to estimate the degradation of \( G_o \) as a function of \( \bar{C}_{HF} \). The derived dependence is also plotted on Figure 4-4 (dotted line). It reveals a very good agreement with the experimentally measured \( G_o \), and might serve as a predictive correlation for the estimation of the degradation level in \( G_o \) for a large range of contaminant concentration \( C_{HF} \) (or \( \bar{C}_{HF} \)). It should be noted, while Equation (6) is approximate, it provides the basis for the experimentally observed trend of the macroscopic interfacial fracture energy variation with the contamination level. However, more rigorous analysis for the cohesive length scale could provide more accurate expression.
The implications of the proposed correlations in Equations (3) and (6) are far reaching. They would provide an assessment of the current state of the intrinsic adhesion and the effective interfacial fracture toughness with prior knowledge of the initial adhesive properties of the pristine surface and its current mechanical properties, defined by Young’s modulus and flow stress. The level of contaminant concentration can be assessed by spectroscopic methods [17]. The mechanical properties of the adhesive layer can be estimated from a small and presumably non-destructive nano- or micro-indentation on the surface [21]. Such methodology might provide plausible pathway to assess the reliability of adhesively bonded joints exposed to contamination. Though, it has to be verified to other adhesive/adherend systems.

**Summary**

In summary, the measured effective interfacial toughness and the estimated interfacial surface energy exhibited correlations with the level of the surface contaminant concentrations. The interfacial fracture surface topology exhibited ductile-to-brittle transition with the increase of the contaminant concentration. These correlations were developed from the modified Gibbs adsorption equation and the principals of large scale bridging in fracture mechanics. The proposed predictive correlations revealed very good qualitative and quantitative agreement with the experimentally measured and numerically calibrated values. The derived correlations can provide a framework to predict the contamination-induced degradation of interfacial surface and macroscopic fracture energy for varying level of surface contamination. Such framework might represent the basis for non-destructive evaluation of bond line integrity by assessing the adsorbed species level, for similar interface
roughness. As the initial interface topology and geometric roughness have significant effect on the macroscopic fracture toughness [28].

References


CHAPTER 5. CORRELATING INREFACIAL FRACTURE TOUGHNESS TO SURFACE ROUGHNESS IN POLYMER-BASED INTERFACES

A manuscript prepared for publication in a journal.

Denizhan Yavas, Ashraf F. Bastawros
Department of Aerospace Engineering, Iowa State University, Ames, IA 50011-2271

Abstract

This study reveals a correlation between the interfacial toughness and the resulting fracture surface roughness for a polymer-based interface. The variation of the interfacial toughness is achieved through varying levels of interfacial contamination. The macroscopic interfacial toughness is measured by double cantilever beam test. Statistical fracture surface analysis is performed by utilizing 1D height-height correlation function. The roughness exponent of the self-affinity does not show a noticeable dependence on the interfacial toughness ($\beta \approx 0.35 \pm 0.04$). The cut-off length scale, the upper bound of the self-affine domain, exhibits a linear correlation with the resistance of the interface to the crack growth. The linear correlation is attributed to the reduction of the process zone size imposed by the degradation of the interfacial fracture toughness. Similarly, the fracture surface RMS roughness reveals a gradual reduction with the decreasing interfacial toughness. The presented correlation has potential for the utilization of the statistical characterization of the fracture surfaces to estimate the interfacial toughness.
Fracture toughness of a material has been defined as material’s resistance to crack growth. In a simplistic view of Griffith's theory, it is the required surface energy for the creation of new free surfaces. The microstructure of a material is one of the main determinants of material’s resistance to crack growth. In general, the microstructure controls the crack growth path, and thereby the fracture toughness by altering the newly created fracture surface area. Accordingly, the fracture surfaces contain many unique features at different length scales, which generally provide substantial information on damage initiation and propagation. The fracture surface morphology can be quantitatively characterized in terms of many different parameters, such as root mean square (RMS) roughness amplitude, roughness exponent of self-affinity, fractal dimension [1]. The self-affine nature of fracture surfaces was firstly introduced by Mandelbrot [2] using a new definition called “fractal”, which is used to describe the surface irregularities. The fractal dimension was mathematically formulated in terms of the slope of the self-affine domain, which is later named as the roughness exponent ($\beta$). Then, Mandelbrot et al. [3] presented a negative correlation between the fractal dimension of the fracture surface and the material’s Charpy impact toughness for a steel. This study has been commonly considered as the first attempt for such correlation, and followed by many other studies providing similar correlations for variety of materials [4-7]. However, the recent studies have shown that the roughness exponent (or fractal dimension) is independent of the examined material and its toughness, provided that the same failure mode is maintained [8-12]. A universal exponent was conjectured to be $\beta \approx 0.8$ for a common range of materials and failure mechanisms [8-11].
The universality of the surface roughness exponent hindered the utilization of statistical fracture surface analysis for quantitative characterization of damage or failure. Alternatively, the cut-off length scale of the self-affine domain ($\xi$) was utilized as a unique length scale to characterize the microscale fracture process [13-15]. It was shown that $\xi$ correlates with the process zone (PZ) size within the crack tip vicinity, thereby with the work of fracture [15]. For example, Bonamy et al. [13] showed an inverse correlation between $\xi$ and crack growth velocity, that is inversely proportional to the PZ size, for a quasi-static brittle fracture. In addition, Ponson et al. [15] have numerically presented a linear correlation between $\xi$ and the material toughness for ductile failure, as long as $\xi$ characterizes the microscale failure process. They also interpreted $\xi$ as a typical length scale for the largest roughness features on the mean fracture plane. However, there hasn’t been a study showing a similar correlation for interfacial fracture, even though the scaling properties of interfacial fracture surfaces were studied extensively [16].

This study is a naïve attempt to explore a plausible correlation between fracture surface roughness and interfacial fracture toughness for a polymer-based interface. The interfacial fracture toughness was altered by varying concentration of a chemical contaminant (MIL-PRF-87257). The double cantilever beam (DCB) tests were used to characterize the interfacial macroscopic (effective, $G_{eff}$) fracture energy for the varying level of contaminant concentration. The DBC samples were constructed bonding two carbon fiber-reinforced composite laminates by 400mm thick adhesive layer (Hysol EA9394). The examined adhesive is an amine-cured with aluminum powder inclusions. The chemical contaminant was unfirmly applied on the adherend panel surfaces prior to the bonding process. The details of the sample preparation and DCB testing procedure can be found
elsewhere [17, 18]. A summary of measured interfacial toughness is presented in Figure 5-1, as a function of the applied contaminant concentration on a logarithmic scale. The control level (uncontaminated) of the interfacial toughness is presented as the shaded region with dashed lines, with ±STDEV interval. As anticipated, the measured $G_{\text{eff}}$ was found to be progressively reduced with the increase in the level of contaminant concentration. In fact, we recently showed that the degradation trend follows an Arrhenius-type correlation between interface toughness and contaminant concentration [19].

Figure 5-1  Summary of effective fracture toughness measurements as a function of contaminant concentration in log-scale, highlighting the severe chemical degradation of the interfacial toughness. The reference fracture toughness level for the uncontaminated bond line is presented by the shaded area, with ±STDEV interval. The insert shows a scanning electron microscope image of the adhesive material, revealing the aluminum powder particles size embedded in the adhesive.
Method and Results

Following the DCB fracture experiments, the fracture surfaces of the samples were scanned by 3-D non-contact surface profiler (Zygo NewView™ 6300). The profiler uses principles of phase-shifting interferometry, which can provide up to 20 nm vertical resolution. The field of view of fracture surface scans was selected to be 1.45x1.45 mm² with a sampling array of 992x992 pixels². With the selected field of view and sampling image array, inter-point lateral resolution of 1.46 μm was obtained. The field of view was determined considering three characteristic length scales associated with the examined material system: (1) the weave periodicity of the adherend panels (~3 mm), (2) adhesive film thickness (~400 μm), and (3) the average size of aluminum powder fillers embedded in the adhesive material (40 μm). First, the visual inspection of the fracture surfaces showed that the wavelength of the fracture surface topology is imposed by the adherend panel texture (the fabric weave periodicity). This observation was found to be independent of the interfacial toughness level. Therefore, the scan area was selected to be about half of the fabric weave periodicity. Second, the adhesive layer thickness represents the relevant length scale for the interfacial adhesion process zone size [20-22]. For a sufficiently thick adhesive layer, fracture process zone is typically smaller than adhesive layer thickness. It was verified that the selected scan area is adequately large to capture the plastic process zone and surface morphology associated with the plastic deformation of the adhesive layer. Lastly, the material heterogeneities have a subtle effect on the fracture properties of materials, and resulting morphology of cracks and fracture surfaces. [23]. The scaling properties of fracture surface such as the roughness exponent have exhibited a strong dependence the analysis
domain. Therefore, the analysis domain size has to be chosen carefully considering the heterogeneity size. This fact was taken into account so that the scan size can provide an appropriate analysis domain.

![Figure 5-2](image)

**Figure 5-2** The change in fracture surface RMS roughness measured over 1.45x1.45mm² area for varying effective fracture toughness. The insert optical images show the crack propagation profile and the corresponding fracture surface for two different interfacial toughness level, revealing the variation of smoothness of the fracture surface with the interfacial roughness.

As the first quantitative indicator, the root mean square (RMS) surface roughness, $R_{RMS}$, of the fracture surfaces was measured and presented in Figure 5-2 for varying $G_{eff}$.

Figure 5-2 shows a linear correlation between the RMS roughness and interfacial toughness. The optical insert images show the interfacial crack profile and corresponding fracture surface morphology for two different interfacial toughness level ($G_{eff} \approx 780\ J/m^2$ and $110\ J/m^2$).
For $G_{\text{eff}} \approx 780 \, \text{J/m}^2$, the interfacial crack profile exhibits a very irregular crack path, whereas it becomes much smoother with the reduced interfacial toughness $G_{\text{eff}} \approx 110 \, \text{J/m}^2$. The correlation in Figure 5-2 is directly reflected on the interfacial crack profile.

Figure 5-3 Scanning electron microscope images of fracture surfaces for (a) the reference case, revealing a roughened fracture surface with hackle marks on the fibers, and (b) the most severe (55µg/cm²) contamination case, showing a smoother fracture surface with a thin layer of residual adhesive on the fibers. The dashed arrows indicate the crack propagation direction.

A similar variation in the fracture surface morphology was observed at the microscale level. Figure 5-3 shows scanning electron microscope (SEM) images of the fracture surfaces for $G_{\text{eff}} \approx 780 \, \text{J/m}^2$ and 110 J/m². The fracture surface of the tougher interface exhibits a step-like ridges. Figure 5-3(a) shows a region nearby one of these ridges on the fracture surface. The average height of these step-like ridges was measured to be about 50µm.
from independent non-contact interferometry measurements. Existence of such surface morphology is direct manifestation of mixed-type (cohesive + adhesive) failure for the tougher interface. In addition to that, the fracture surface depicts very distinctive features within the adhesive and cohesive failure zones. For example, the adhesive surface (in the cohesive failure zone) exhibits striation marks with enhanced roughness at finer scale, while the substrate surface (in the cohesive failure zone) shows hackle marks on the fibers. The presence of striation and hackle marks are vivid evidences of improved energy absorption mechanisms at micro-scale. Overall, such surface morphology can be linked with the strong interfacial strength and the resulting enhanced plastic (or inelastic) deformation of the adhesive layer. However, the fracture surface of the sample with lower interfacial toughness exhibits a glassy surface, with a very thin adhesive layer covering the entire substrate surface. The glassy appearance is an indication of brittle fracture, resulting in low interfacial toughness. The residue of thin adhesive layer suggest that the interfacial crack grows along the interface, signifying cohesive-type failure. Therefore, the reduced interfacial strength and fracture toughness can prevent the adhesive layer from plastic deformation and thereby lead to the observed surface morphology.

Figure 5-4 shows 3-D rendering of the fracture surface topologies for the three different levels of $G_{eff}$, along with typical height profiles in the crack growth direction. The sampling of the fracture surfaces was performed over the steady-state crack growth regimes for all examined cases. The repeatability of the measurements was verified by multiple scans over the same surface. The statistical surface analysis was carried out for a comparable set of data for the examined cases. The scanned fracture surfaces were quantitatively characterized using 1-D height-height correlation function along the crack growth direction. The height
variation of the fracture surface was calculated using the correlation function $\Delta h(\Delta x)$ defined as,

$$\Delta h(\Delta x) = \sqrt{\left\langle \left( h(x+\Delta x) - h(x) \right)^2 \right\rangle_x}$$

(1)

where $\langle \cdot \rangle$ denotes the averaging over the $x$-direction. The correlation functions were evaluated for each pixel-line along the $x$-coordinate. Then, they are used to obtain the averaged correlation function with reduced low frequency noise. Figure 5(a) shows log-log plots of the correlation function $\Delta h(\Delta x)$ for the three different $G_{\text{eff}}$ levels. Within the self-affine domain, at relatively smaller length scales ($\Delta x \leq 50 \mu m$), the correlation curves follow a power law behavior ($\Delta h \sim \Delta x^{\beta}$) regardless of the interfacial toughness level. The roughness exponent, the slopes of the correlation curves within the self-affine domain, was calculated to be $\beta = 0.35 \pm 0.04$ for the examined cases. The computed $\beta$ is much lower than the universally reported value, $\beta \approx 0.8$. Such discrepancy can be attributed to the nature of the interfacial fracture. A similar value $\beta = 0.4$ was reported in case of interfacial fracture of two PMMA plates [16]. In addition, the recent studies have reported relatively small values within the range of $\beta = 0.4 - 0.5$ for different materials such as glass [24] and sandstone [25].

The correlation curve of the fracture surface with $G_{\text{eff}} \approx 780 \text{ J/m}^2$ exhibits an inflection point with two different roughness exponents within the self-affine domain, though these two values are very close to each other. This behavior can be attributed to the secondary roughness arising from the mixed-type failure observed for the toughest interface. At relatively higher length scales ($\Delta x \geq 50 \mu m$), the correlation curves start to saturate and exhibit a plateau at different $\Delta x$ values, presenting an upper bound for the self-affine
behavior. The critical length scale \( (\Delta x)_{\text{critical}} \) is defined as the cut-off length scale \( (\xi) \) of the self-affine nature \( (\xi = (\Delta x)_{\text{critical}}) \).

Figure 5-4  3D rendering of the fracture surface topologies along with the typical height profiles along crack propagation direction (sampled along \( y=0.25\text{mm} \) line) for the three different levels of the toughness. The arrows represent the crack growth direction.
Figure 5-5  (a) A representative set of height-height correlation functions along the crack propagation direction for the three different level of toughness, showing the self-affine nature within the smaller length scales with the roughness exponent $\beta = 0.35 \pm 0.02$ independent of the toughness value, and the upper bound of the self-affinity defined as the cut-off length scale $\xi$. (b) the correlation between the cut-off length scale and the measured effective bond line toughness for the examined cases.
Interestingly, the cut-off length scale, $\xi$, was found to be monotonically decreasing with the decreasing $G_{\text{eff}}$. The variation of $\xi$ with $G_{\text{eff}}$ is presented in Figure 5-5(b), showing a linear correlation between $\xi$ and $G_{\text{eff}}$. This correlation is in a good agreement with the correlation between $R_{\text{RMS}}$ and $G_{\text{eff}}$ presented in Figure 5-2. Accordingly, $\xi$ can physically be interpreted as a length scale correlating with the fracture surface roughness. As can be seen in Figure 5-5(b), $\xi$ was measured to be $\xi \approx 340 \mu m$ for the interface with $G_{\text{eff}} \approx 780 \text{ J/m}^2$, which is comparable with the adhesive layer thickness ($t_{\text{adhesive}} \approx 400 \mu m$). Hence one can link $\xi$ with the plastic process zone size within in the adhesive layer. Whereas, for the interface with $G_{\text{eff}} \approx 110 \text{ J/m}^2$, $\xi$ is limited to be $\xi \approx 70 \mu m$, which is attributed to the restricted process zone size as a result of limited plastic deformation of the adhesive layer with the decreasing $G_{\text{eff}}$. Such argument can also be rationalized using principals of the interfacial fracture mechanics, as discussed in the next paragraphs.

**Discussion**

The macroscopic interfacial toughness, $G_{\text{eff}}$, is controlled by many different factors. For example, the previous work [20-22] showed that the adhesive thickness can significantly alter $G_{\text{eff}}$ by controlling the adhesive plasticity and plastic dissipated energy. Therefore, $G_{\text{eff}}$ can be expressed as the confluence of different forms of energy such that [26, 27],

$$G_{\text{eff}} = G_0 + \dot{W}_p + \dot{W}_v + \Delta G$$

(2)
where \( \left( \cdot \right) \) denotes the derivative with respect to the change in the crack area, \( \left( \cdot \right) = d( \cdot )/dA \).

\( G_0 \) is the intrinsic cohesive toughness (work of adhesion) of the interface, and \( \dot{W}_p \) is the rate of plastic (or inelastic) energy dissipation in the vicinity of crack tip, \( \dot{W}_v \) is the rate of bulk viscoelastic dissipation in within the adhesive layer, and \( \Delta G \) is the additional fracture energy arising from shielding due to the fracture surface roughness of the interface. Contributions of \( \dot{W}_v \) and \( \Delta W \) to \( G_{\text{eff}} \) were shown to be highly dependent of the mode mixity. Considering the mode-I fracture conditions, \( \dot{W}_v \) and \( \Delta W \) are anticipated to be negligible compared to the first two terms \( G_0 \) and \( \dot{W}_p \) in Eq. (2) [28, 29].

The plastic energy dissipation within a plastic zone occupying a volume \( V_p \) is given by,

\[
W_p = \left( \int_{V_p} \int_0^{\sigma_y} \sigma \, d\sigma \, dV \right) - W_e
\]

where \( W_e \) is the elastic strain energy, and assumed to be relatively smaller than the first integral term in Eq. (3) in the vicinity of the crack tip (within the volume \( V_p \)). In addition, within the volume \( V_p \), one can assume full yield conditions such that \( \sigma_y \approx \sigma \), and estimate a strain state such that \( \varepsilon_y^0 \approx n\hat{\sigma}/E \), where \( n \) is the hardening exponent, and \( E \) the Young’s modulus of the adhesive layer, and \( \hat{\sigma} \) is the interfacial strength. Assuming a perfectly rectangular plastic zone shape for sake of simplicity [30], the rate change of \( W_p \) per unit crack extension over the sample width, \( b \), can be formulated as,
\[
\dot{W}_p = \frac{W_p}{b\Delta a} \approx \sigma, \left(\frac{n\bar{\sigma}}{E}\right)(R_p)
\]  
\(\text{(4)}\)

where \(R_p\) is the plastic process zone size in front of the crack front. An important length scale, \(R_0\) for \(R_p\) is given as follows [26],

\[
R_0 \approx \frac{1}{3\pi} \left(\frac{K_0}{\sigma_y}\right)^2 = \frac{1}{3\pi(1-\nu^2)} \frac{E G_0}{\sigma_y^2}.
\]  
\(\text{(5)}\)

where \(\nu\) is the Poisson’s ratio of the adhesive layer. \(R_0\) generally represents an approximate length scale for the plastic process zone size under small scale yielding (\(R_p \approx R_0\) if \(G_{\text{eff}} \approx G_0\)). Therefore, using Equations (2-5), the overall interfacial toughness can be written as follows,

\[
G_{\text{eff}} \approx \left[1 + \frac{n}{3\pi(1-\nu^2)} \left(\frac{\bar{\sigma}}{\sigma_y}\right)\right] G_0
\]  
\(\text{(6)}\)

Comparing Equations (5) and (6), both \(R_p\) and \(G_{\text{eff}}\) are linearly proportional to \(G_0\) for the fixed mechanical properties of the adhesive. This suggests that \(R_p\) is proportional to \(G_{\text{eff}}\), as well as, to \(\xi\), since the linear correlation between \(\xi\) and \(G_{\text{eff}}\) was experimentally shown.

Figure 5-6 shows the variation of \(\xi\) with \(R_0\). Here, \(R_0\) values are evaluated by Equation (5) using \(G_0\) values numerically obtained for each \(G_{\text{eff}}\) level and the adhesive properties \(E = 4.3\text{GPa}, \nu = 0.43, \sigma_y = 69\text{MPa}\). The details of numerical calibration of \(G_0\) can be found in Ref. [17]. \(R_0\) is found to be an order of magnitude lower than the \(\xi\) (\(\xi/R_0 \approx 13\)). Such discrepancy can be attributed to significant plastic dissipation within the adhesive layer.

If \(G_{\text{eff}} > G_0\), then the process zone size is anticipated to be larger than the provided length.
scale, $R_p > R_0$. For the examined material system and geometry, $G_0$ was predicted to be smaller than $G_{eff}$ ($G_{eff} / G_0 \geq 2$) [19]. Therefore, $R_0$ can only be regarded as a scaling length, rather than an absolute value, for the plastic process zone size. The observed correlation supports that $\xi$ presents a relevant length scale for the interfacial process zone size, and be alternatively used to predict the overall effective interfacial toughness $G_{eff}$, provided that $G_{eff} > G_0$.

Figure 5-6 (a) The variation of the estimated length scale for the process zone size ($R_0$) with the measured interfacial toughness, (b) the predicted correlation between $R_0$ and $\xi$. 
Conclusion

In conclusion, this study investigated the interfacial fracture surfaces of a typical polymer-based adhesive by utilizing statistical fracture surface analysis employing 1D height-height correlation function. We showed that; (i) the roughness exponent of the self-affine domain is independent from the interfacial toughness ($\beta \approx 0.35 \pm 0.04$), (ii) the estimate length scale for the PZ size provided a linear correlation with the cut-off length scale of the self-affine behavior, (iii) accordingly the interfacial effective fracture toughness was found to be scaling with the cut-off length scale, which is also interpreted as the roughness indicator of the fracture surface. The presented correlation shows potential for the utilization of the statistical characterization of the fracture surfaces to estimate the interfacial toughness. The presented correlations are expected to provide the basis for the development of the statistical characterization of the interfacial fracture surfaces.

References


CHAPTER 6. MORPHOLOGY AND STRESS EVOLUTION DURING THE INITIAL STAGES OF INTERGRANULAR CORROSION OF X70 STEEL

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Denizhan Yavas\textsuperscript{a}, Abdullah Alshehri\textsuperscript{b}, Pratyush Mishra\textsuperscript{c}, Pranav Shrotriya\textsuperscript{b}, Ashraf F. Bastawros\textsuperscript{a}, and Kurt R. Hebert\textsuperscript{c}

\textsuperscript{a}Department of Aerospace Engineering, Iowa State University, Ames, IA, 50011, United States
\textsuperscript{b}Department of Mechanical Engineering, Iowa State University, Ames, IA, 50011, United States
\textsuperscript{c}Department of Chemical and Biological Engineering, Iowa State University, Ames, IA, 50011, United States

Abstract

Pipeline steels are vulnerable to stress corrosion cracking (SCC) during intergranular corrosion (IGC) at potentials of active dissolution in moderately alkaline carbonate-bicarbonate solutions. Morphology evolution accompanying IGC has not been fully described, despite the relevance of the corrosion geometry to crack initiation. The present article reports a characterization of concurrent morphology and mechanical stress development during the initial stages of IGC of X70 steel in sodium bicarbonate solution, in the potential range of high SCC susceptibility. Morphology was revealed by scanning
electron microscope examination of cross sections through the IGC layer, and stress
evolution was monitored by curvature interferometry. At potentials in the range of SCC
susceptibility, IGC creates triangular wedges of porous corrosion product centered at grain
boundary triple junctions. The wedge shape indicates a higher corrosion rate at the grain
boundary compared to the grain surfaces. Compressive stress is generated during IGC due to
internal oxidation on grain surfaces forming a thin compact corrosion product layer.
 Polarization at a potential below the SCC range resulted in selective grain dissolution with no
internal corrosion product or compressive stress increase. Silicon solute atoms are selectively
oxidized into the compact grain boundary corrosion product film.

**Introduction**

Pipeline steels are susceptible to both intergranular stress corrosion cracking (SCC)
and intergranular corrosion (IGC) in “high-pH” (i.e. pH 8-10) carbonate-bicarbonate
solutions [1, 2]. IGC and SCC occur at the same pH values, and in the same well-defined
range of potentials within the active dissolution peak of the steel polarization curve [3-7].
The equivalent conditions for SCC and IGC suggest that the corrosion process itself is
directly responsible for grain boundary embrittlement. Mechanisms proposed for corrosion-
induced embrittlement have included formation of geometric features such as notches that
concentrate external stress, or creation of brittle surface layers or films on corroding surfaces
[8]. Much of the prior research on intergranular corrosion of pipeline steels has concerned the
nature of electrochemical corrosion reactions and products within the critical potential range
[9-15]. It is found that dissolution near the potential of the active dissolution current peak
produces Fe(II) hydroxide and carbonate species, while at potentials above the active region
insoluble Fe(III) products are found. Also, the potential ranges of both IGC and intergranular SCC has been shown to lie between the active peak and the passivation potential, in which both Fe(II) and Fe(III) products are formed. However, this work did not not establish a relationship between the electrochemistry of corrosion within the critical potential range and the SCC mechanism. Also, no prior work to our knowledge focused on the role of grain boundaries in the corrosion process, which is clearly central to an understanding of intergranular SCC.

Because of the close coupling between intergranular corrosion and stress corrosion cracking of pipeline steels, it is important to identify aspects of corrosion at grain boundaries that are relevant to the evolving mechanical properties of the near-surface region. Corrosion morphology development is potentially significant because the geometry of the corroded region determines its response to external tensile stress. Further, intergranular corrosion rates can be inferred by observing grain boundary morphology evolution. Despite the relevance of intergranular corrosion to high-pH SCC of pipeline steels, no detailed characterization of grain boundary morphology evolution during IGC of ferritic steels has been reported in the literature, in contrast to the knowledge base about such processes on austenitic stainless steels [16]. Also, it has been proposed that corrosion-induced wedging stress at grain boundaries can assist crack initiation and growth [17-20]. However, very few studies exist on stress evolution accompanying corrosion along grain boundaries. Recently, we reported a nanoindentation study of corroded X70 pipeline steel which suggested that corrosion directly induces mechanical property changes at grain boundaries [21, 22]. The experiments revealed 1 μm-thick mechanically degraded layers adjacent to corroded grain boundaries with 25% lower hardness relative to the grain interior. Further knowledge of corrosion reactions at
grain boundaries is needed to understand the origin of grain boundary softening and its relation to SCC.

The present study focuses on morphology and mechanical stress evolution during high-pH intergranular corrosion of X70 pipeline steel in sodium bicarbonate solution. Scanning electron microscope (SEM) examination of cross sections through the IGC-affected subsurface layer were used to characterize the spatial distribution of metal dissolution and corrosion product formation in relation to the grain microstructure, at potentials within the range of highest SCC susceptibility. It is found that within the critical potential range, IGC produces triangular wedges of corrosion product around grain boundary triple junctions. The wedge shape is due to local enhancement of the corrosion rate on the grain boundary itself relative to the grain surfaces. Mechanical stress evolution during corrosion was monitored using in situ stress measurements and related to internal oxidation within the IGC layer.

**Experimental Details**

Samples of a high strength low-alloy pipeline steel (API X70) were machined from a pipe wall. The specimens of 1 mm thickness were cut along the long axis of the pipe, with the top surface in the longitudinal-short transverse plane. The sample length and width dimensions were 18 x 18 mm². The main alloying elements in X70 were Mn (~1.75 wt. %), Si (~0.45 wt. %), and C (~ 0.17 wt. %). The minority pearlite phase was composed of grains less than 5 μm in width and elongated in the longitudinal direction, while the majority ferrite phase was made up of nearly equiaxed grains of typically 5 μm size. The sample surfaces were polished with 400, 600 and 800-grit sandpaper, followed by cleaning with deionized water and ethanol. Electrochemical experiments were carried out in a three-electrode cell
with Pt wire counter electrode and Ag/AgCl reference electrode. All cited potentials are with respect to this reference. The test solution was naturally aerated aqueous 1 M NaHCO$_3$ at room temperature. Solutions were prepared using analytical grade reagents and deionized water (resistivity 18 MΩ-cm). The applied potential was first held at -1.0 V for 5 min to cathodically reduce surface oxide, and then stepped or scanned in the anodic direction.

For examination of the corrosion morphology in cross section, samples were polished to reveal planes at orientations either perpendicular to or at a shallow angle from the surface. Corrosion specimens were examined by scanning electron microscopy (SEM, FEI Quanta 250), and by non-contact optical profilometry (Zygo NewView 6200). In addition, focused ion beam (FIB) microscopy was utilized to reveal corrosion morphology, using an ion beam at 52° from the surface (FEI NanoLab Helios Dual Beam). A 1 µm thick and 15 µm long protective carbon strip was first deposited on the sample surface in order to preserve the top corrosion product layer. Then, a trench with an area of 25x25 µm$^2$ was ion-milled with a depth of about 5 µm. Finally, a finer ion-milling step with a reduced material removal rate was performed normal to the top surface to reveal the corrosion cross section.

In situ stress measurements employed the phase shifting curvature interferometry method [23]. The applications of this technique to measure stress changes during corrosion and anodic oxidation of aluminum were described in earlier publications [20, 24]. One side of the steel sample was polished to a 0.05 µm particle finish using a diamond particle suspension and served as a reflective surface for interferometry. The specimen was mounted in a test cell with the unpolished side in contact with the electrolyte solution and the opposite side facing the optical system. Changes in sample curvature during corrosion were
monitored. The curvature change \( (d\kappa) \) is related to the near-surface force per width \( (dF_w) \) according to the Stoney thin-film approximation,

\[
dF_w = \frac{E_s h_s^2}{6(1 - \nu_s)} d\kappa
\]

where \( E_s, \nu_s, \) and \( h_s \) are respectively the elastic modulus, Poisson's ratio and thickness of the steel sample. The force per width is the in-plane biaxial stress \( \sigma_{xx} \) integrated through the sample thickness,

\[
F_w = \int_0^{h_s} \sigma_{xx} dz
\]

where the \( x \) axis is parallel to the steel surface, and the \( z \) axis extends toward the bulk metal from its origin at the surface. Force per width is referenced to the initial state of the sample at the beginning of anodic polarization. Compressive and tensile force changes are respectively negative and positive in sign.

**Results and Discussion**

**Electrochemical Measurements**

Figure 6-1(a) shows the active dissolution region of the polarization curve of X70 steel in 1 M NaHCO\(_3\) solution. The potential region of susceptibility to IGC and SCC extends from the potential of the current peak at -0.6 V to the passivation potential at -0.4 V [4, 6, 7]. Three test potentials within this range were selected for potentiostatic experiments, as indicated in the Figure: -0.575 V, -0.521 V and -0.478 V. Examples of current transients at these potentials are shown in Figure 6-1(b). Initially, the current density decayed to a
minimum value at 1 - 6 min at all three potentials. From rotating ring-disk electrode (RRDE) experiments Riley and Sykes found that the main reaction during the current decay is formation of a surface film [13]. Based on the charge density of 10 to 30 mC/cm² passed during the decay, the equivalent Fe(OH)₂ thickness is 14 - 40 nm, comparable to the thickness of 80 nm from XPS for the steady-state surface film at the peak potential [14]. At the two higher potentials, the current increased to a maximum after the initial decay and then slowly fell. No maximum was reached after 45 min at -0.575 V.

Figure 6-1  Electrochemical measurements during corrosion of X70 steel in 1 M NaHCO₃. (a) Linear sweep voltammetry showing the three test potentials used in other experiments. (b) Current density transients for the experiments used for morphology observations in Figs. 4-7.
Large-angle Cross-section Samples

Large-angle cross section views of the steel interface after corrosion tests at -0.521 V for 2h and 4h are exhibited in Figures 6-2(a) and 6-2(b), respectively. The 2h-exposed sample was prepared by FIB milling and the 4h sample by cross-sectioning and mechanical polishing. The along the top surface Both images illustrate the corrosion product film that covered the steel surface after the current density maximum. The white-shaded material is the steel and the dark gray-shaded layer on its upper surface is corrosion product. The corrosion product consists of particles several 𝜇m in width separated by small gaps. The void in the central part of the film in Figure 6-2(a) is atypical and may be caused by attrition of a corrosion product particle during sample preparation. EDS of the corrosion product layer in Figure 6-2(b) revealed that it contained Fe, O and C, suggesting that the film is an iron hydroxy-carbonate as found previously [10, 14, 15]. The Na/Fe concentration ratio of 0.15 indicated that the product contained significant amount of sodium, consistent with the finding of sodium or potassium in the corrosion product in earlier studies [10, 15]. Incorporation of electrolyte Na⁺ ions is evidence that the product is formed by precipitation. Nanoindentation measurements revealed an elastic modulus of 28 GPa for the product layer, much smaller than the value of about 200 GPa for dense iron oxide [22, 25]. The low modulus of the film suggests high porosity, also consistent with a precipitated film.

The precipitated corrosion product layer thickness measured from the cross-section images increased from 2.5 𝜇m at 2h to 4.3 𝜇m at 4h. The corresponding ratios of thickness to charge density were 1.9 x 10⁻⁴ cm³/C at 2h and 1.6 x 10⁻⁴ cm³/C at 4h. These values can be compared to the ratios associated with possible product layer constituents. The corrosion product formed in bicarbonate solutions is an iron hydroxycarbonate [15], which at
-0.521 V may contain both and Fe(II) and Fe(III) compounds [9, 10, 13, 14]. The thickness-charge density ratio for compact product layers based on the molar volumes of Fe(OH)$_2$, FeCO$_3$ and Fe(OH)$_3$ are respectively $1.4 \times 10^{-4}$, $1.5 \times 10^{-4}$ and $9.5 \times 10^{-5}$ cm$^3$/C. The porosity of the product layer is consistent with the somewhat larger ratios found experimentally.

Figure 6-2  Large-angle cross section views after corrosion at -0.521 V. (a) 2 hr exposure; sample prepared by FIB etching, cross section plane $52^\circ$ from horizontal. (b) 4 hr exposure; sample prepared by polishing, cross section plan $90^\circ$ from horizontal. Dashed lines indicate triangular wedge features produced by corrosion at the alloy-corrosion product interface. The angles of the wedge apex are marked in the image.

The images in Figure 6-2 reveal a number of triangular wedges along the metal-corrosion product interface, marked by dashed lines. The wedges are positioned close to the
gaps between corrosion product particles. These features were especially evident during FIB examination for Figure 6-2(a), as numerous wedge features located at different points on the surface appeared and disappeared as the sample cross section was ion-milled. The wedge angle is defined as shown in Figure 6-2 as the angle at the apex of the triangular groove. Based on about 8 measurements at each exposure time, the wedge angle was $136 \pm 6.4^\circ$ at 2 hr and $117 \pm 17^\circ$ at 4 hr. The wedge depths are about $0.6 \mu m$ at 2h and 1 to $1.5 \mu m$ at 4h. Triangular wedges can be produced by intergranular attack, as discussed in the next section.

Figure 6-3  Height profile measured by optical profilometry after 2 hr exposure at -0.521 V and followed by removal of corrosion product. Curve to the left of the arrow represents an area that was not exposed to solution.

Figure 6-3 exhibits a non-contact optical topological scan for an experiment in which the sample was exposed for 2h at -0.521 V. After the experiment, the corrosion product was removed by wiping the surface with a swab dipped in acetic acid. The profile spans parts of the rough corroded surface as well as surrounding surface (abscissa values smaller than 10
μm) that was not exposed to solution. The corroded area reveals minima with depths from 0.3 to 0.7 μm below the uncorroded area, and peaks that rise above the surrounding surface. The minima are apparently the triangular wedges marked by dashed lines in Figure 6-2(a), as both features have the same range of depths and similar lateral spacing. The peaks are likely remnants of corrosion product particles. If these particles are disregarded, the top surface heights inside and outside the corroded area are the same. It can therefore be concluded that there was no significant general corrosion on the surface between the triangular wedges. A similar profile measured after 4h (not shown) also supports the absence of general corrosion. Thus, despite the overall appearance of the product layer as a uniform film, the corrosion process seems to exclusively consist of localized attack centered at shallow triangular wedges.

**Small-angle Cross-section Samples**

Small-angle cross sections were prepared by polishing to reveal the internal corrosion morphology on planes nearly parallel to the external surface. Figure 6-4 exhibits SEM images of a steel specimen after a 2h corrosion exposure at -0.521 V. The current density transient for the same experiment is found in Figure 6-1(b). In the low magnification image in Figure 6-4(a), the intergranular corrosion layer lies between the precipitated corrosion product and uncorroded base alloy. The layer labeled corrosion product in Figure 6-4(a) is the same as the precipitated iron hydroxide-carbonate layer noted in Figure 6-2. Note that distances along the vertical direction in these images magnify depth through the polishing angle. The magnification factor in this direction is approximately 1000, since the apparent thickness of the IGC layer in Figure 6-4(a) is 900 μm, while the FIB cross section (Figure 6-
2(a)) reveals the true IGC layer thickness to be 0.9 μm. Figures 6-4(b)-(e) are higher-magnification views at selected depths within the IGC layer. Figures 6-4(d) and 6-4(e) illustrate that localized corrosion attack centers at grain boundary triple junctions between the equiaxed and approximately 5 μm diameter steel grains. Black-shaded crevices formed by corrosion at triple junctions are surrounded by roughly 1 μm thick gray-shaded corrosion product layers coating the white-shaded steel grains. In addition to progressing along the triple junctions, corrosion also penetrates laterally along the grain boundaries adjacent to the triple junctions (Figure 6-4(d)). At the interface between the metal and the top corrosion product layer (Figure 6-4(c)), the grain boundary product film surrounds isolated clusters of grains. The cores of these grain clusters are eventually converted to corrosion product, forming the particles comprising the film. Thus, the corrosion product morphology reflects that of the underlying grain structure.

The crevices along triple junctions in Figure 6-4 correspond to the fissures at the triangular wedges in Figure 6-2. Therefore, Figures 6-4(c)-(e) represent respectively the top, midpoint and apex of the triangular wedges in Figure 6-2. Note that triple junction crevices are present in Figure 6-2 only when the cross section plane lies close to the wedge apex. Since the triangular wedges are centered at triple junctions, they are indeed associated with intergranular attack. Triangular wedges have been observed during intergranular corrosion of austenitic stainless steels at transpassive potentials, and are considered to be characteristic features of “unsensitized” IGC in the absence of grain boundary precipitates [16, 26]. The wedge angle \( \alpha \) is related to the ratio of the dissolution velocity of the grain boundary at the wedge apex \( V_{gb} \) to the wedge surface dissolution velocity \( V_s \).
\[ \frac{V_{gb}}{V_s} = \frac{1}{\sin(\alpha/2)} \]  

Figure 6-4  Small-angle cross section views of X70 steel after 2 hr corrosion at -0.521 V. Sample was prepared by shallow-angle polishing. Panels (b) - (e) are high-magnification images at the points indicated in the low-magnification image (a).
The wedge angles in the present work suggest $V_{gb}/V_s$ of 1.1 - 1.2, much smaller than the ratio of approximately 10 indicated by the relatively acute wedge angles in stainless steel [16]. To our knowledge, the triangular wedge morphology of IGC in pipeline steel has not been previously noted. However, Wendler-Kalsch found that corrosion in the potential range of SCC susceptibility produced 2 μm-deep grain boundary grooves similar in appearance to the wedges in Figure 6-2 [5]. No such grooves were observed in Ref. [5] at potentials higher than the upper limit of the SCC potential range, suggesting that the fundamental processes that produce the grain boundary wedge shape may intrinsically important in the SCC mechanism.

Figure 6-5  Schematic depiction of triangular wedge morphology of intergranular corrosion.

The important features of the intergranular corrosion geometry are depicted schematically in Figure 6-5, which shows the triangular wedge morphology at the corroded triple junction. The wedge angle $\alpha$ and the corrosion velocities $V_s$ and $V_{gb}$ are defined. Figure
6-5 also illustrates the precipitated porous corrosion product layer in Figures 6-2 and 6-4(a), and an underlying compact layer between the precipitate and the steel. Evidence for such a nonporous corrosion product was obtained by nanoindentation measurements, which revealed submicron-thick regions close to the metal with elastic modulus approaching that of compact iron oxide [21, 22].

Figure 6-6  Composition of grain boundary corrosion product film on sample exposed for 2 hr at -0.521 V. (a) SEM showing location of EDS line scan. (b) Composition profile along the line scan.
Figure 6-6 shows an EDS line scan across a corroded grain boundary in a sample exposed for 2h at -0.521 V. The major species in the corrosion product layer are iron, oxygen and carbon, consistent with a product layer composed of iron hydroxy-carbonates [15]. The composition is close to that of the top surface corrosion product but without significant levels of sodium deriving from NaHCO₃ electrolyte. According to Blengino et al., product layers exhibit variable quantities of incorporated electrolyte ions depending on the corrosion rate [15]. Manganese, the primary alloying element in X70 steel, is apparently selectively excluded from the product layer, while silicon from the alloy is selectively oxidized and incorporated into the product. Silicon can significantly affect IGC in austenitic stainless steels, but we know of no prior reports of silicon effects on IGC or SCC of pipeline steels, or evidence for selective oxidation of Si at grain boundaries in X70 [16, 27]. Prior analytical TEM measurements of X52 and X65 steels revealed grain boundary segregation of only Mn solute, and atom probe tomography showed evidence for C segregation in X52 and X70 steels [28-30].

Additional small-angle cross sections were prepared on a sample exposed at -0.521 V for 15 min. At these early times, the cross sections revealed scattered corrosion product particles and isolated evidence of grain boundary attack at triple junctions, consistent with previous observations [13, 15]. Therefore, the current rise during polarization at constant potential (Figure 6-1(b)) correlates with spreading of intergranular attack to an increasing fraction of the surface grain boundaries. This interpretation was suggested previously by Riley and Sykes [13]. Similar current transients with maxima were recently found during CO₂ corrosion of carbon steel near pH 6, and the current rise was interpreted differently in
terms of voids caused by crystallite nucleation in an amorphous surface film, or pH decrease due to carbonate precipitation [31, 32].

Figure 6-7 Small-angle cross section views of X70 steel after 2 hr corrosion at -0.478 V. Sample was prepared by shallow-angle polishing. Panels (b) and (c) are high-magnification images at the points indicated in the low-magnification image (a).

Figure 6-7 exhibits small-angle cross sections of steel exposed at -0.478 V for 1 hr, for which the current density transient is given in Figure 6-1(b). Figure 6-7(a) shows the entire thickness of the IGC layer, while Figure 6-7(b) represents the interface between steel and the top product layer, and Figure 6-7(c) shows the midsection of the corroded region. As
at -0.521 V, corrosion at -0.478 V is localized at triple junctions, and extends into lateral grain boundaries surrounding the triple junctions. Comparison of the interface images Figure 6-7(b) and Figure 6-4(c) reveals that, despite the smaller exposure time at -0.478 V, there is a significantly larger number density of corroded grain boundary triple junctions at the higher potential, and consequently greater penetration of corrosion product between grains.

Apparently, the rate of spreading of IGC among grain boundaries increases with potential, correlating with the faster increase of current density with time after the initial minimum (Figure 6-1(b)).

![Small-angle cross section views of X70 steel after 2 hr corrosion at -0.575 V. Sample was prepared by shallow-angle polishing. Panels (b) and (c) are high-magnification images at the points indicated in the low-magnification image (a).](image)
Figure 6-8 shows small-angle cross sections for a 50 min corrosion experiment at a potential of -0.575 V, close to the active dissolution peak of the steel polarization curve. The susceptibility of steel to SCC is considered to be lower at such potentials in comparison to potentials closer to the passivation potential [4]. The images in Figure 6-8 represent an area near a deposit of corrosion product, which in this experiment covered only a small portion of the surface. Figure 6-8(a) shows the entire thickness of the IGC layer, Figure 6-8(b) the steel-product layer interface, and Figure 6-8(c) shows the midsection of the corroded region. In contrast to the two more positive potentials, the cross-sectional images at -0.575 V revealed almost no detectable internal corrosion product at grain boundaries. Instead, IGC is characterized by selective dissolution of grains.

**Transient Electrochemical and Stress Measurements**

In this section, in situ stress measurements during intergranular corrosion are presented and discussed in view of the observations of IGC morphology evolution. Figure 6-9(a) displays current density and force per width transients from experiments at each of the three test potentials, and the charge density obtained by integration of the current is shown in Figure 6-9 (b). Force per width at -0.478 V and -0.521 V increased steadily in the compressive direction during polarization. After an initial compressive period at -0.575 V, the force changed direction at 9 min, and exhibited a net tensile change at 60 min. From the trends in Fig. 9, it is clear that compressive stress generation correlates with internal corrosion product formation: extensive grain boundary corrosion product was found at the two higher potentials, but none at -0.575 V.
Figure 6-9  Stress and current density measurements during corrosion exposures at the three test potentials. (a) Force per width (solid lines) and current density (dashed lines) transients. (b) Charge density transients obtained by integrating the current density in (a).

Stress is produced during oxide layer formation by strain associated with the volume increase upon conversion of metal to oxide [33]. The same principle can be applied to the present hydroxide-carbonate layers. As a first approximation, stress is modeled in a flat
nonporous corrosion product film of uniform thickness, which comprises an inner dense layer between the metal and an outer stress-free porous precipitated corrosion product (Figure 6-5). As mentioned above, the presence of this compact layer was revealed by nanoindentation measurements [21, 22]. Since adherence of the surface film with the metal requires compatibility of the net in-plane strain at the metal-film interface, the formation of the compact layer must result in elastic or plastic strain within the film. It is assumed that the oxidation-induced strain-thickness product of the film is isotropic and hence given by \( \Delta V_{mjf}/3 \), where \( \Delta V_{mjf} \) is the net volume expansion per unit area at the metal-film interface during metal oxidation [33],

\[
\Delta V_{mjf} = \frac{q \Omega_p}{2F} \left( t_A - \frac{1}{\Phi} \right)
\]  

(4)

Here \( q \) is the anodic charge density, \( F \) is Faraday’s constant, \( \Omega_p \) is the molar volume of corrosion product, \( \Phi \) is the Pilling-Bedworth ratio (the ratio of corrosion product to metal volume), and \( t_A \) is the average transport number for inward electrical migration of \( \text{OH}^- \) and \( \text{CO}_3^{2-} \) anions in the product layer. The anion transport number represents the fraction of current associated with film growth at the metal interface, with the remaining fraction \((1 - t_A)\) due to outward metal ion migration resulting in growth of the precipitated film. In Equation (4), \( t_A \) is the thickness of corrosion product formed at the metal interface per overall layer thickness, and \( 1/\Phi \) is the consumed metal thickness per product layer thickness.

Assuming hypothetically that the strain in the product layer is elastic in nature, the force per width would be given by

\[
F_w = \frac{E_s \Delta V_{mjf}}{3(1-\nu_s)}
\]  

(5)
Combining Equations (3) and (4), the elastic stress generated is

\[ F_w = \frac{\Omega_p q E_s}{6F(1-V_s)} \left( \frac{1}{\Phi} - t_A \right) \]  

(6)

While \( t_A \) in the product layer is unknown, passive films on iron and steel generally support both cation and anion transport by migration through grain boundaries between nanocrystals [34], and the presence of the outer precipitated product layer indicates that \( t_A \) must be less than unity. For an example calculation, \( t_A \) is taken to be 0.5, with \( \Omega_p \) and \( \Phi \) assigned values of 26.4 cm\(^3\)/mol and 3.7 for Fe(OH)\(_2\). For the maximum charge density of 300 mC/cm\(^2\) in Figure 6-9 (b), the calculated force is close to \(-10^4\) N/m, two orders of magnitude higher than the measured value. Therefore, despite the uncertain transport number, it is likely that the volume expansion due to oxide formation is accommodated by plastic rather than elastic deformation. The yield stress of the compact corrosion product was estimated to be 330 MPa from nanoindentation hardness measurements [22]. At the force levels in Figure 6-9 (a), the compact product layer thickness would be \( F_w/\sigma_y \) of 100 to 200nm where \( \sigma_y \) is the yield stress. This range is compatible with the submicron layer thickness of the compact layer revealed by nanoindentation [22]. Thus, the calculation supports the view that the porous precipitated layer is stress-free.

If the stress in the product layer remains close to the yield stress, the force can be approximated as \( F_w \approx \sigma_y h_p (A_p/A_s) \). Here \( \sigma_y \) and \( h_p \) are the yield stress and thickness of the compact portion of the product layer, \( A_p \) is the area covered by the product layer (i.e. the entire oxidized surface area along grain boundaries) and \( A_s \) is the projected steel surface area. Assuming that the compact layer thickness remains constant, the increase of
compressive force over time is due to increase of $A_p$ as intergranular corrosion spreads over the surface and penetrates into the metal. Thus, the stress measurement is seen to be a sensitive indicator of internal oxidation during intergranular corrosion, arising specifically from the compact product layer and not from the precipitated porous oxide seen in SEM. Indeed, the force transient at -0.575 V suggests oxidation at times less than 10 min, which is not apparent in cross-sectional SEM images at later times. Note that Figure 6-9(a) reveals different time dependence of force and current density at the two higher potentials: while force increases steadily, current density reaches a maximum and then decays. The different trends arise because current density depends on both corroding area and the corrosion product thickness, increasing at first as IGC spreads and decreasing at longer times due to growth of the outer product film.

Relevance to Mechanisms of Intergranular Corrosion and Stress Corrosion Cracking

The present morphological observations reveal that at potentials of -0.521 and -0.478 V in the range of high SCC susceptibility, intergranular corrosion is centered at triple junctions and penetrates into lateral grain boundaries surrounding the triple junction. High-angle cross section images at -0.521 V show that corrosion at triple junctions takes the form of triangular wedges or notches, as illustrated in Figure 6-5. At a potential near the active dissolution peak, the images reveal no precipitated internal dissolution product, and corrosion proceeds by selective grain etching. The shallow wedge shape near the passivation potential is explained by a constant dissolution velocity $V_s$ on the grain surface and a slightly higher velocity $V_{gb}$ at the grain boundary itself (Equation (3)). Stress measurements provide evidence for a compact surface layer at the two higher potentials, which likely regulates $V_s$. 
The mechanism explaining the higher dissolution rate on the boundary is less evident. Open crevices are found along corroding grain boundaries at -0.521 V and -0.478 V (Figure 6-5), and the absence of a porous product would reduce the resistance for mass transport along the boundary. Others have proposed that grain boundary segregated carbon is important for intergranular SCC of low-carbon steels [30, 35]. However, SEM images of shallow angle-polished specimens reveal no evidence for segregated phases at the boundaries. Wedging stresses due to the compact corrosion product layer at the grain boundary could assist corrosion propagation along the boundary [17].

The IGC morphology evolution described here may be related to the strong correspondence between the potential and pH ranges for SCC and IGC [7, 36]. Wendler-Kalsch suggested that wedges produced by corrosion at grain boundaries may induce sufficient stress concentrations to initiate stress corrosion cracks [5]. Indeed, a critical finding of both Ref. [5] and the present work is that wedge or notch features are found only in the potential range where steel is vulnerable to SCC. However, it is not clear that the relatively blunt wedges in Figure 6-2 can generate significant stress concentration to influence SCC. It is possible that notches with smaller angles and hence larger stress concentrations may be produced at longer exposure times, or by synergistic enhancement of intergranular corrosion by external stress [7]. Another possible reason for the importance of grain boundary oxidation in SCC is suggested by the EDS measurements in Figure 6-6 which revealed selective oxidation of Si solute atoms. Preferential oxidation of reactive solutes may produce non-equilibrium metal vacancies, and vacancy-dislocation interaction can explain the reduced local hardness near corroded grain boundaries recently detected by nanoindentation [22, 37]. Since vacancies associated with grain boundary oxidation would be present only at
potentials or high cracking susceptibility, the possible involvement of vacancies in the SCC mechanism should be considered. A third possible role of grain boundary oxidation in SCC is that wedging stresses due to the compact corrosion product layer at the grain boundary could directly assist grain boundary fracture [17].

**Conclusion**

The present article reports characterization of morphology and stress evolution during intergranular corrosion of X70 pipeline steel to aqueous 1 M NaHCO$_3$ solution at pH 8.1. At active dissolution potentials close to the passivation potential, for which the steel is susceptible to intergranular stress-corrosion cracking, IGC produces triangular wedges of porous corrosion product centered around grain boundary triple junctions. The wedge shape is due to a higher corrosion rate at the grain boundary itself compared to that on the grain surfaces. Corrosion penetrates along triple junctions while it also spreads laterally into adjacent grain boundaries. Closer to the potential of the active current peak, intergranular corrosion proceeds by selective dissolution of grains with no evidence of internal oxidation. In situ stress measurements close to the passivation potential revealed compressive stress generation due to formation of a compact corrosion product layer along corroding grain surfaces, but a net tensile stress change at a potential close to the current peak at which no internal oxidation was found. Si solute atoms are selectively oxidized into the grain boundary corrosion product. Overall, the results demonstrate that grain boundary oxidation associated with corrosion product wedges occurs at potentials for which X70 steel is vulnerable to SCC.
References


CHAPTER 7. NANOINDENTATION STUDY OF CORROSION-INDUCED GRAIN BOUNDARY DEGRADATION IN A PIPELINE STEEL

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Denizhan Yavas\textsuperscript{a}, Pratyush Mishra\textsuperscript{c}, Abdullah Alshehri\textsuperscript{b}, Pranav Shrotriya\textsuperscript{b}, Kurt R. Hebert\textsuperscript{c}, Ashraf F. Bastawros\textsuperscript{a}

\textsuperscript{a}Department of Aerospace Engineering, Iowa State University, Ames, IA, 50011, United States
\textsuperscript{b}Department of Mechanical Engineering, Iowa State University, Ames, IA, 50011, United States
\textsuperscript{c}Department of Chemical and Biological Engineering, Iowa State University, Ames, IA, 50011, United States

Abstract

High-strength low-alloy steels used for oil and gas pipelines are vulnerable to intergranular stress corrosion cracking in moderately alkaline soils. The mechanism of corrosion-induced embrittlement under such conditions is not yet understood. Nanoindentation was used to detect localized degradation of mechanical properties near internal grain boundaries of X-70 steel undergoing intergranular corrosion at active dissolution potentials at pH 8.2. The measurements identified a one-micron thick mechanically-degraded layer with 25\% reduced hardness near corroded grain boundaries. It
is suggested that the corrosion process may introduce an active softening agent, possibly non-equilibrium lattice vacancies generated by oxidation.

**Introduction**

Stress corrosion cracking (SCC) refers to the failure by cracking of normally ductile high-strength alloys in a corrosive environment. Stress corrosion cracking is a pervasive concern in energy and transportation sectors; for example, it is responsible for about 21% of steel oil and gas pipeline failures [1]. There is widespread debate about the mechanism through which corrosion leads to reduction of the fracture toughness. Typically, SCC initiates at localized corrosion sites such as pits or grain boundaries (GBs) undergoing intergranular corrosion (IGC) [2]. Intergranular stress corrosion cracking (IGSCC) is thought to involve localized corrosion-induced mechanical property changes at grain boundaries, such as formation of brittle layers or films, or enhanced dislocation motion and nucleation resulting in localized plasticity [3-5]. Localized plasticity is frequently attributed to absorption of hydrogen produced by cathodic reduction of water accompanying corrosion [5, 6]. The present work concerns "high-pH" IGSCC of high-strength low-alloy steels used for pipelines, which occurs in the pH range 8 to 11 in the potential region of active steel dissolution [7-10]. Attention is focused on the nature and mechanism of material property changes during the early development of intergranular corrosion attack that precedes SCC.

Localized changes in material properties near grain boundaries are probed effectively by indentation measurements. Micro-hardness experiments indicate that segregation of solute atoms at the GBs results in either hardened or softened regions compared to the interior of the adjacent grains [11, 12]. Nanoindentation has detected a significant increase in the
intrinsic hardness of the material near the GBs due to dislocation pinning [13-18]. In situ nanoindentation measurements during electrochemical exposures of metals at cathodic potentials revealed near-surface softening due to absorbed hydrogen [19, 20]. However, evidence suggests that embrittlement during high-pH SCC of pipeline steel results from anodic dissolution rather than absorbed hydrogen [21, 22]. Hardness decreases in iron undergoing anodic corrosion have been detected, and were attributed to softening by vacancies injected during metal dissolution [23]. However, to our knowledge no prior study has measured local corrosion-induced material property changes at grain boundaries, which are critically relevant to the mechanism of IGSCC. The present communication reports locally resolved ex situ nanoindentation measurements at corroded grain boundaries in X70 pipeline steel, in the pH and potential ranges of maximum SCC susceptibility. The measurements reveal evidence for degradation of hardness near GBs. These are apparently the first observations of local corrosion-induced softening of grain boundaries under conditions associated with high SCC susceptibility.

**Experimental Details**

The alloy under investigation was a high strength pipeline steel (API 5L X70) with average grain size of 5 μm. The major alloying elements are Mn (~ 1.75 wt %), Si (~ 0.45 wt %), and C (~ 0.17 wt %). Samples 2 mm in thickness and 18 mm x 18 mm in cross-section were machined from the pipe wall. The sample surface was polished with 400, 600, and 1000-grit grinding papers, then cleaned by deionized water and ethanol prior to experiments. Electrochemical experiments were performed in a cell with a Pt wire counter electrode and Ag/AgCl reference electrode. All reported potentials are relative to the Ag/AgCl reference.
Naturally aerated 1 M NaHCO₃ electrolyte solutions with pH 8.2 were prepared from analytical grade reagents and ultra-pure water (resistivity 18.2 MΩ-cm). In corrosion experiments, the applied potential was first held at -1.0 V for 5 min to cathodically reduce surface oxide, and then stepped to a test potential within the active dissolution peak of the polarization curve.

After corrosion exposures, the steel samples were polished at a shallow angle from the horizontal to expose the near-surface region affected by intergranular corrosion. Quasi-static indentations were performed using a Hysitron TI 950 TriboIndenter with 90° cube corner indenter tip under force control with 250 µN peak, thereby limiting the indentation profile to the initial sink-in range [24, 25]. The tip radius was about 300 nm, making the whole indent within the spherical tip nose. Accordingly, the corresponding process zone under the indenter tip was estimated to be about 500 nm, which was utilized as the indent spacing. The intergranular corrosion morphology was characterized by scanning electron microscopy (SEM), Focused Ion Beam (FIB) Microscopy (FEI Helios NanoLab DualBeam) and atomic force microscopy (AFM) mode of the TriboIndenter system. The thickness of the corrosion product layer on the steel surface was measured by a non-contact optical profilometer (Zygo NewView 6300).

**Results and Discussion**

X70 steel is most susceptible to IGSCC at potentials between the current peak for active metal dissolution and the passivation potential [21, 22]. Potential sweep experiments at a scan rate of 1 mV/s identified the active peak potential to be -0.600 V, and the passivation potential was approximately -0.400 V. Accordingly, potentiostatic experiments were
performed at the intermediate potential of -0.521 V. Figure 7-1(a) shows a typical anodic dissolution current density transient at this potential. The current decreased to a minimum at 5 min, then rose to a peak of 0.35 mA/cm² at 30 min, after which it slowly decayed.

Microscopic examination revealed scattered corrosion product particles prior to the current maximum, while after the maximum a continuous product layer covered the surface. Riley and Sykes suggested that current density increases to maxima in similar experiments might be due to initiation and spreading of IGC [26]. The current density decay after the maxima is apparently associated with growth of the corrosion product layer [27].
Figure 7-1(b) shows a SEM image of a shallow angle polished section of a sample corroded for 2h. Three distinct layers can be identified: a top corrosion product layer, a near-surface intergranular corrosion layer, and uncorroded base alloy. According to energy dispersive X-ray analysis, the corrosion product layer contained Fe, C and O atoms, suggesting that it includes iron hydroxide and possibly carbonates (as the extent of carbon contamination is not clear) [27]. It should be noted that dimensions along the vertical direction in Figures 7-1(b)-(d) correlate with depth through the shallow polishing angle. FIB cross sections revealed that the thickness of the IGC layer was about 0.9 μm, indicating that depth in Figure 7-1 is magnified by a factor of 1000, the ratio of the apparent IGC layer thickness (900 μm) to the true thickness. The IGC morphology at two depths is illustrated in Figures 7-1(c) and 7-1(d). These images reveal white-shaded equiaxed steel grains with IGC attack initiating at triple junctions between grains. The corroded steel surface on the grain boundary is covered by a gray-shaded, ~ 1 μm thick corrosion product layer, which according to EDS consists of iron hydroxide and possibly carbonate. Additionally, corrosion has opened central voids or crevices in the grain boundaries between the corrosion product layers. In the part of the IGC layer close to the base alloy (Figure 7-1(d)), many grain boundaries are apparently filled or nearly filled with corrosion product. At intermediate depths in the IGC layer (Figure 7-1(c)), the crevice width increases while the corrosion product film thickness remains at about 1 μm.

Nanoindentation experiments were carried out to detect degradation of material properties in the vicinity of corroded grain boundaries. The indents were arranged along four lines perpendicular to the GB and traversing the boundary at different distances from the crevice at a triple junction (Figure 7-2(a)). Line 1 is close to the crevice, while line 4
intersects the boundary about 1.6 µm beyond the crevice. Typical load-indentation depth curves are shown in Fig. 2 (b) for the indents at distances 0.25 µm and 1.75 µm from the GB on line 3. Within the initial elastic part of the loading curve, both curves follow Hertzian spherical contact [28], then exhibit incipient of plasticity at different loading levels (marked by the displacement bursts).

![AFM image and force-indentation depth curves](image)

Figure 7-2  (a) AFM image in surface gradient mode showing the grain boundary and the locations of the imposed lines of nanoimprints. (b) A representative set of force-indentation depth curves for the indents on line 3 at distances 0.25 µm (blue) and 1.75 µm (green) from the GB within grain 1. The dashed line shows the Hertzian fit for spherical indenter tip.

The corresponding indentation hardness, $H$, and elastic modulus, $E$, were extracted from force-displacement curves (Figure 7-2(b)) using the Oliver-Pharr method [29]. Figure 7-3 illustrates the variation of $H$ and $E$ along each line of indentations. The parameters are plotted vs. lateral distance to the approximate position of the GB, which is marked by dashed lines in Figures 7-2(a) and 7-3. We first note a slight difference in the average $H$ and $E$ in the interior of the grain on either side of the GB, due to the probable difference in crystallographic orientation between the two grains. The measured $H$ values are higher than
those for macroscopic bulk measurements, because of the well-known phenomenon of indentation size effect [30, 31]. Figure 7-3(a) shows the variation of $H$ and $E$ on lines 1 and 2 of Figure 7-2(a) near the tip of the crevice. A marked drop in both quantities can be observed compared to the grains on either side of the GB. The measured modulus and hardness are about 35 GPa and 1.7 GPa respectively. This region likely corresponds to the grain boundary corrosion product, since independent measurement of the product layer properties on the exposed steel surface showed comparable values of $E \approx 28\pm8$ GPa and $H \approx 1.5\pm0.4$ GPa. The low modulus value is consistent with a porous iron oxide; as dense oxide should have a modulus around 200 GPa [32]. The layer with reduced $E$ and $H$ extends about 0.7 $\mu$m on either side of the GB, consistent with the average chemical product layer thickness around the GB in Figures 7-1(c) and 7-1(d). Beyond this domain of low modulus, there is a transition zone which extends to a distance of about 1 - 1.5 $\mu$m on either side of the GB. The intermediate $E$ and $H$ values in the transition zone may result from the combined influences of the adjacent corrosion product layer and grain interior.

Figure 7-3(b) shows the variation of $H$ and $E$ along line 3 of Figure 7-2(a), where the corrosion crevice approaches a tighter, fully closed state. The reduced modulus region is much narrower than those in lines 1 and 2, with a thickness of about 0.5 to 0.75 $\mu$m from either side of the boundary. Note that since the grain boundary position marked by the dashed line is only approximate, the grain boundary may actually intersect the midpoint of the reduced modulus layer, i.e. at about -0.4 $\mu$m in Figure 7-3(b). This position would be consistent with equal product layer thicknesses on each side of grain boundaries indicated in Figure 7-2. The reduced modulus $E$ is in the range 130 to 170 GPa, similar to that of a dense iron oxide [32]. In contrast to the modulus, the hardness distribution shows a significantly
wider range of reduced $H$ that extends over a distance of about 1.5 - 1.75 $\mu$m from either side of the GB. The level of recorded hardness is about 75 % that of the interior of the grain. Such a band with reduced hardness, but with a modulus consistent with that of the bulk, was quite repeatable for other examined GBs on the angle-polished cross-section. In addition, a similar trend was found when examining the top corroded surface by direct indentation measurements after removal of the top oxide layer with dilute acetic acid solution [33].

![Graph showing variation of hardness $H$ and modulus $E$ across the GB for the indentation lines 1, 2 (a), line 3 (b), and line 4 (c) in Figure 7-2. CP designates corrosion product.](image)

Finally, Figure 7-3(c) shows the variation of $H$ and $E$ along line 4 of Figure 2 (a), which is located further along the GB from the corrosion crevice. Within the lateral resolution of the measurements, neither distribution in Figure 7-3(c) reveals layers with altered properties along the grain boundary. Instead, both $E$ and $H$ show sharp transitions
between the bulk grain values of $E \approx 198$ GPa and $H \approx 5.15$ GPa for the grain on the left side to $E \approx 180$ GPa and $H \approx 4.15$ GPa in the right-hand grain. Apparently, line 4 is beyond the deepest penetration of grain boundary corrosion, resulting in the absence of corrosion product or degraded metal layers. Similar trends have been observed on 7 measurements of different grain boundaries on this sample and on 3 repeated corrosion experiments, showing the average softer layer total thickness of about $2.0 \pm 0.25 \mu m$. It should be noted that scatter range was dictated by the indent separation rather than the stochastic variability of the assessed soft-layer thickness. The average reduction of the soft layer hardness was about $23 \pm 3.5\%$ from the reference level of the bulk of the grain. Therefore, it is concluded that the micron-wide steel layer with reduced hardness at line 3 is associated with the corrosion process. Such a degraded steel layer would not be detectable closer to the triple junction (lines 1 and 2), because its indentation response would be masked by that of the thick corrosion product.

Localized plasticity in the reduced hardness layer could result in embrittlement due to dislocation pile-up at the outer edge of the plastic zone, in a similar fashion as the hydrogen-induced local plasticity (HELP) mechanism for hydrogen embrittlement [5,19,20]. Absorbed hydrogen might not be the softening agent in the present corrosion process, however, since SCC susceptibility correlates strongly with anodic steel dissolution and not cathodic hydrogen formation [21, 22]. Degradation of mechanical properties can be associated with thin diffusion layers in the metal adjacent to the corroding surface [34,35]. Also, anodic dissolution might leave behind clusters of atomic vacancies that diffuse into the steel, and have been considered as a driver for softening behavior [23, 36]. Guo et. al. showed that electrochemical dissolution-induced degradation of iron might be plausibly explained by the
generation of non-equilibrium vacancies in the subsurface layer, possibly associated with oxidation of reactive solute atoms [22]. Molecular dynamics simulation showed that increase of vacancy concentration can lead to decrease of the dislocation nucleation load in iron [36]. Despite uncertainty about the precise degradation mechanism, the observed corrosion-induced grain boundary softening is mechanistically relevant to stress corrosion cracking, as it occurs in the potential and pH range of highest susceptibility of X70 steel to IGSCC.

Summary

In summary, the present nanoindentation measurements show that corrosion of X70 steel in pH 8.2 at active dissolution potentials results in a mechanically degraded layer near internal surfaces of corroded grain boundaries. Nanoindentation revealed about 25 % drop in hardness in the degraded layer, with no measurable change in the elastic modulus. It is suggested that a softening agent produced during corrosion at grain boundaries may account for reduction of dislocation barriers, such as non-equilibrium vacancies injected by oxidation. These findings provide a possible mechanism of corrosion-induced steel embrittlement during the early stages of intergranular stress corrosion cracking.

References


CHAPTER 8. A COMBINED EXPERIMENTAL AND ATOMISTIC STUDY OF GRAIN BOUNDARY DEGRADATION INDUCED BY CORROSION GENERATED VACANCIES

A manuscript prepared for publication in a journal

Denizhan Yavas\textsuperscript{a}, Thanh Phan\textsuperscript{a}, Liming Xiong\textsuperscript{a}, Kurt R. Hebert\textsuperscript{b}, Ashraf F. Bastawros\textsuperscript{a}

\textsuperscript{a}Department of Aerospace Engineering, Iowa State University, Ames, IA, 50011, United States

\textsuperscript{b}Department of Chemical and Biological Engineering, Iowa State University, Ames, IA, 50011, United States

Abstract

A combined experimental and atomistic computational analyses of the grain boundary (GB) degradation in X-70 pipeline materials under active dissolution potentials at pH 8.2 was performed in this work. Experimental nanoindentation measurements revealed a gradual decrease in the critical load for incipient plasticity within one-micron vicinity of GBs. In parallel, atomistic simulations were conducted and the active softening agent responsible for the detected GB degradation were determined. Results suggested that (1) vacancies, rather than interstitial hydrogen-atoms, generated by intergranular corrosion promotes dislocation nucleation, which in turn, results in GB degradation; and (2) the degradation level at GBs is
controlled by the vacancy concentration, varying with the relative distance to GBs according to Fickian diffusion law.

**Introduction**

Stress corrosion cracking (SCC) is a failure process in materials under combined effect of tensile stress and corrosive environment. The localized corrosion sites such as grain boundaries (GBs) in materials are typically active pathways for corrosion initiation. In particular, the segregation of point defects, such as hydrogen interstitials or vacancies makes GBs highly susceptible to commencement of intergranular stress corrosion cracking (IGSCC) [1]. To quantify the IGSCC-induced material property degradation, ex-situ nanoindentation experiments [2] were recently performed to measure the material hardness of X70 pipeline steels in an aggressive environment. A significant degradation of mechanical properties arising from intergranular corrosion activities was found in the vicinity of GBs. In parallel, to reveal the atomistic mechanisms of the experimentally-observed GB degradation, many molecular dynamics (MD) simulations of crystalline iron which was charged with either atomic-level vacancies or hydrogen interstitials, under indentation were also conducted [3-6].

Simulation results suggest that there are two main sources, (1) non-equilibrium lattice vacancies, (2) interstitial hydrogen atoms, responsible for the observed localized mechanical property changes in metallic materials under an electrochemical attack. However, in spite of the extensive efforts above [7-20], how an IGSCC initiates at a fundamental level is still not fully understood up to date with a variety of mechanisms among several under debating: (i) the hydrogen enhanced localized plasticity, in which the dislocation mobility near GBs is considered to be promoted by the absorption of hydrogen from the cathodic reduction of water [7-16]; (ii) the hydrogen induced accumulation of excess vacancies, which lead to the
formation of brittle zones nearby the GBs [17-20]. In this work, nano-indentation tests were conducted to characterize the local constitutive responses of the materials near the GBs in pipeline steels undergoing an active dissolution within a pH range of 8~11. The experiment results are directly compared with the MD simulation of indentation of crystalline iron containing vacancies and hydrogen interstitials. The major softening agent that controls the experimentally-observed gradual GB degradation is identified.

**Experimental Details and Observations**

A high-strength pipeline steel (API 5L X70) was taken as the model material in this work. The samples with a dimension of 2 mm in thickness and 18×18 mm² in cross-section were machined from the pipe wall, with the top surface in the longitudinal-short transverse plane. The majority of the surface composed of ferrite phase with nearly equiaxed grains of 5μm size. The sample surface was polished with 400, 600, and 800-grit grinding papers, then cleaned by deionized water and ethanol prior to electrochemical exposure. Electrochemical experiments were performed in a cell with a three electrode cell with Pt wire counter electrode and Ag/AgCl reference electrode. All reported potentials are with respect to this reference. Naturally aerated 1M NaHCO₃ electrolyte solutions with pH 8.2 were prepared from analytical grade reagents and ultra-pure water (resistivity 18.2 MΩ-cm). The applied potential was first held at -1.0 V for 5 min to cathodically reduce native surface oxide, and then stepped to a test potential within the active dissolution peak of the polarization curve (-0.521 V vs Ag/AgCl) [21]. After chemical exposures, the steel samples were polished at a shallow angle to reveal the internal IGC morphology on a plane nearly parallel to the top
surface. Figure 8-1(a) depicts a scanning electron microscope (SEM) of IGC morphology within the IGC-affected layer. The image reveals white-shaded base material grains, which are surrounded by roughly 1 µm thick gray-shaded corrosion product layers. IGC attacks at the triples junctions shown as black-shaded regions in Figure 8-1(a).

![SEM image of the polished surface, showing the IGC attach at the triple junctions, (b) AFM image in surface gradient mode showing the grain boundary and the locations of the imposed lines of nanoimprints, (c) A representative set of force-indentation depth curves for the indents on line 2 at different distances from the GB, along with Hertzzian fit for spherical contact. (d) The summary of critical load for the first displacement burst (normalized by the critical loads obtained for the interior of the grains), presented as a function of distance from GB.](image_url)
The observed enhanced corrosion activity at GBs suggests a substantial degradation of the mechanical properties in the vicinity of the GBs. To quantify plausible GB degradation, quasi-static nanindentations were performed on the polished surface using a Hysitron TI 950 TriboIndenter with a 90° cube corner diamond indenter tip under force control with 250 µN peak, thereby limiting the indentation profile to the initial sink-in range [22]. The tip radius was independently profiled by scanning nano-patterned calibration grating (NT-MDT) to be about 350 nm. The large tip radius facilitates the whole indents within the spherical tip nose, with the maximum indentation depth less than 40 nm. Accordingly, the radius of the corresponding process zone under the indenter tip was estimated to be less than 500 nm [23], which was utilized as the indent spacing.

Figure 8-1(b) is an atomic force microscope (AFM) surface topography image, showing a crevice at a triple junction, with two lines of nanoimprints perpendicular to the GB. The imposed two lines traversing the GB at two different distances from the triple junction. Line 1 is close to the crevice, where a layer of GB oxide exists. While line 2 intersects the grain boundary at a distance about 1.6 µm. Figure 1(c) shows a set force-indentation depth curves obtained at different distances from the GB (the letters correspond the positions in Fig. 1(b)). The fully elastic response of the base material using Hertzian contact theory was also provided in Fig. 1(c). Considering the elastic loading of two spherical elastic model [23], the indentation load, $P$ is related to displacement, $h$ as follows,

$$P = \frac{4}{3} E R^{1/2} h^{3/2}$$  \hspace{1cm} (1)

where $E$ is the indentation modulus ($E \approx 210 GPa$) and $R$ is the tip radius of the indenter, considering as a sphere ($R \approx 350 nm$).
In the early stage of the deformation for shallow indentation depths up to 1-2 nm, all curves exhibit a very similar response and follow the Hertzian response. Thereafter the curves corresponding to the indents placed closer to the GB (C and D) start deviating from the elastic response at about 2 nm depth (corresponding to a loading level 20 μN), while such deviation takes places at a slightly larger depth (6 nm, corresponding to a loading level of 60 μN) for the indentation placed closer to the interior of the grain. The measured load (or displacement) corresponding to the observed deviation from the elastic response can be associated with the critical load required for incipient of plasticity [24-26]. In addition, as can be clearly seen, all curves exhibit multiple “displacement bursts” occurring at a constant load level. These displacements burst events have been linked with several different mechanisms such as such as dislocation generation or migration [24-26], brittle cracking of native oxide layer [27], surface roughness [28].

In the current experiments, a special care was taken to ensure that the surface roughness is significantly smaller than the indenter tip radius. The average geometric roughness (R_a) for each indentation site was measured to be R_a ≤ 5nm over 200×200 nm². Therefore, the first displacement burst event can be attributed to homogenous dislocation nucleation (HDN), as the critical stress is reached underneath the indenter tip [24-26]. The critical stress required to nucleate a homogenous dislocation loop, \( \tau_{HDN} \), can be associated with the maximum shear stress underneath the indentation surface, \( \tau_{max} \), which is a function of the critical load producing the first displacement burst event, as follows [24],

\[
\tau_{HDN} \approx \tau_{max} \approx \tau_{burst} = 0.31 \left( \frac{6 \ E^2}{\pi^3 R^2 P_{burst}} \right)^{1/3}
\]
where $P_{\text{burst}}$ is the measured load corresponding to the first displacement burst.

Meticulous inspection of Figure 8-1(c) reveals an interesting trend in the critical load required for the first significant displacement burst. The observed trend was summarized in Figure 8-1(d), showing the normalized critical load as a function the indent position relative to the GB for two grains. The load values are normalized by that of the grain interior. The critical load, $P_{\text{burst}}$ tends to gradually reduce with the decreasing lateral distance to the GB. There is about 55-60% drop detected in $P_{\text{burst}}$ nearby the GB, which means about 25% degradation in the barrier stress level for HDN (or dislocation mobility). The observed trend was found to be very repeatable within 1-1.5 mm vicinity of the different GBs with multiple nanoindentations performed at different positions on the surface. It should also be noted that the nanoindentation of the base material exhibited an increase in the critical load for incipient plasticity in the vicinity of the GBs. This increase was attributed to dislocation pile-up at GBs [29].

The nanoindentation measurements, within the lateral resolution of the measurements, detected 1.0-1.5μm thick mechanically degraded layer in the either side of the GBs. The material within this zone exhibited lower barrier force (or stress) for HDN (or dislocation mobility), leading to enhanced plasticity. The level of the measured degradation was found to be gradually varying with respect to the relative distance to GBs. We suggest that there may be two probable sources causing to the observed degradation trend near by the GBs. Therefore, an atomic study is carried out to understand the degradation mechanism.

**Atomistic Computational Setup and Results**
Molecular dynamics simulations were performed on a simulation cell of single BCC crystal iron with a dimension of 150 x 150 x 75 Å, which encloses approximately 143,312 atoms (Figure 8-2(a)). The atomistic simulator, LAMMPS [30], was employed here. The FS Embedded Atom Method potentials developed by Mendelev et al. [31] and Ramasubramaniam et al. [32] were utilized for the interaction between iron-iron atoms and iron-hydrogen atoms, respectively. The results were analyzed using Dislocation Analysis Tool in OVITO [33]. Different vacancy concentrations (in atomic percentage) were accomplished by random deletion of Fe atoms in the perfect lattice. Figure 2(a) shows the white atoms around the vacancies for 1% concentration. On the other hand, interstitial H atoms were randomly introduced into the lattice only at the particular interstitial sites [32, 34]. For each concentration, 6 different initial configurations were generated and analyzed to present the statistical variation in the results. Prior to the indentation step, a relaxation step at 1K were performed for all simulations for 50ps, under NVE ensemble. The low temperature facilitates immobility of the initially introduced vacancies. The periodic boundary conditions (PBCs) were used along the x and y directions, while the non-periodic and shrink-wrapped boundary conditions were used along the z direction. The atoms within the bottom layer of the model with thickness of 10 Å were fixed.

The nanoindentation simulations were performed using a rigid spherical indenter with radius R=50 Å up to indentation depth 20 Å, under the NVE ensemble. The temperate was initially set to 1K, and very small temperature fluctuations were recorded with a peak of 3K during the indentation. The indentation axis was chosen to be along the [0 0 1] direction. The initial contact position of the indenter was maintained at the center of the simulation cell. The indenter applies a force of magnitude on each atoms as
\[ F(r) = \begin{cases} -K(r-R)^2, & r < R \\ 0, & r \geq R \end{cases} \tag{3} \]

where \( K = 10eV / A^2 \) and \( r \) is the distance between the centers of indenter and atoms. The indenter speed 5m/s was applied with time step of 2fs, considering the vibrational frequencies of the Fe atoms. It should be noted that the indentation speed of the simulations is relatively high comparing to the experiments, though it is sufficiently low to maintain the equilibrium state in the simulations and achieve qualitatively good results.

Figure 8-2 (a) MD simulation box, showing the iron atoms (blue), and the atoms surrounding the lattice vacancies. (b) load-indentation depth curves for different vacancy concentration. (c) load-indentation depth curves for different hydrogen atom concentration. (d) The summary of the critical load for the dislocation nucleation (normalized by the that of the perfect crystal) as a function of the concentration, along with the experimental results.
Figure 8-2(b) shows the load-indentation depth curves for three different vacancy concentration, along with the curve for the perfect crystal. The initial elastic response of the crystal revealed a gradual softening with the increase of the atomic vacancy concentration, though such variance can be perceived as very insignificant. All curves exhibit a load drop at different loading levels, which occurs due to the dislocation formation in the lattice. Thereby, these loading levels can be defined as the critical load for the incipient plasticity. As can be clearly seen, the critical load tends to decrease with increasing vacancy concentration. In addition, the magnitude of the load drops decreases with increasing vacancy concentration, which can be attributed to enhanced stability of dislocation nucleation with the existence of more atomic vacancies in the lattice.

On the other hand, Figure 8-2(c) depicts the load-indentation depth curves for the same atomic concentrations with the hydrogen insertion in the interstitial sites in the perfect crystal. All cases exhibit relatively softer response in the initial elastic part of the curves comparing to the perfect lattice, whereas there is not a clear correlation between the initial lattice stiffness and the H-atom concentration. Interestingly, unlike the vacancies, interstitial H-atoms in the crystal do not significantly affect the critical load for dislocation formation. A similar trend was observed with the double sized model for both cases, which eliminates concerns of the geometric size effect on the observed trends.

Figures 8-3(a)-(c) depict snapshots of the atomistic configuration underneath the indentation site for the perfect crystals, highlighting the nucleation (a) and propagation (b, c) of the dislocation. All atoms are colored according to the Dislocation Analysis Tool in OVITO where atoms in white are not in perfect crystal. Here the atoms in perfect bcc crystal are not displayed to show dislocations nucleation and propagation. The first dislocation loop
nucleates underneath the indenter tip, where the maximum shear stress reaches the theoretical strength of the lattice. The depth of the nucleation site is approximately 52% of the contact radius $a$, which is in good agreement with the depth $0.48a$ predicted by Hertzian analysis of spherical contact [23]. Figures 8-3(d)-(f) show the corresponding normalized von misses stress fields on (1 0 0) plane, which also supports the same argument. The first dislocation loops form at a location, where a maximum stress maximum shear stress occurs (Figure 8-3(d)). Then dislocation loops propagate with local stress concentration at the dislocation center (Figure 8-3(e)-(f)).

Figure 8-3 (a-c) Snapshots of the atomistic configuration showing the dislocation nucleation and mobility for the perfect crystal, highlighting the dislocation nucleation taking place right underneath the indenter tip. (d-f) the corresponding von misses stress field underneath the indenter tip on (1 0 0) plane.
Figure 8-4  (a-c) Snapshots of the atomistic configuration showing the dislocation nucleation and mobility for the 0.1% vacancy case, highlighting the nucleation of the dislocation loop near by a vacancy cluster.  (d-f) the corresponding von misses stress field underneath the indenter tip on (1 1 0) plane.

On the other hand, Figures 8-4(a)-(c) show snapshots of the atomistic configuration underneath the indentation site for the 0.1% vacancy case. Unlike the former case, the first single dislocation loop nucleates near by a vacancy away from the indenter tip on (1 1 0). The depth of the nucleation site is approximately  84% of the contact radius $a$ in this case. The corresponding normalized von misses stress fields on (1 1 0) plane are presented in Figures 8-4(d)-(f). As can be seen from Figure 8-4(d), one of the vacancies acts as a stress
concentrator, which facilities dislocation nucleation at lower loading level compared to the perfect crystal. It should be also noted that the perfect crystal exhibits multiple dislocation formation during a comparatively short time period, whereas there is typically single loop formation observed for the different vacancy concentrations. Such observation can be linked with the elastically stored energy in the lattice prior to the dislocation formation. The perfect crystal can store relatively more energy, which leads to formation of multiple dislocations. This is also in agreement with the observed trend in the magnitude of the load drops of the load-indentation depth curves. Corresponding to a relatively larger load drop, the perfect crystal releases relatively more energy to facilitate the multiple dislocation formation.

Figure 8-2(d) summarizes the normalized critical load as a function of the concentration for both vacancy and H atom insertion cases, along with the experimental results. The experimental critical load data as a function spatial position from the grain boundary is presented as a function of vacancy concentration, $C$ by utilizing the diffusion equation,

$$C(x,t) = C_0 + \left(C_B - C_0\right) \left[1 - \text{erf}\left(\frac{x}{2\sqrt{D_t t}}\right)\right]$$  \hspace{1cm} (4)

where $x$ is the distance relative to the GB, $t$ is the charging time, $C_0$ is the intrinsic vacancy concentration, $C_B$ is the vacancy concentration in the grain boundary, and $D_t$ is the diffusion coefficient for vacancies in BCC Fe. The boundary concentration was assumed to equal to Si concentration in the base metal, $C_B = 0.5 \text{ atm.\%}$, as the vacancy formation is anticipated to be arising from the selective dissolution of Si atoms [2]. While the initial vacancy concentration was approximated to be nearly zero, $C_0 = 0$. The room temperature vacancy diffusivity was
projected to be about \( D_v = 5 \times 10^{-17} \text{ m}^2 / \text{s} \) using the Arrhenius parameters provided by Mendelev and Mishin [35]. Then the distance \( x \) is converted to \( C(x) \) using Eq. (4) for grain boundary dissolution time of \( t = 2h \). Surprisingly, the variation of the critical load with the increasing vacancy concentration exhibits a good agreement with the experimental measurements. The critical load level exhibits up to 60% drop with about 1% vacancy concentration in the lattice. However, H-atom insertion causes an insignificant decrease in the critical load for the examined concentration range.

Considering the qualitative agreement between the experimental and atomistic simulation results, it can be suggested that non-equilibrium vacancies generated by the corrosion process at GBs are more susceptible for the experimentally observed GB softening. This conclusion is also consistent with electrochemical point of view, since SCC susceptibility is strongly associated with anodic steel dissolution and not cathodic hydrogen formation [36]. The experimentally detected gradual degradation of mechanical properties near GBs can be linked with a thin diffusion layer in the metal adjacent to the corroding surface [17-20]. The clusters of atomic vacancies within such diffusion layer is believed to be generated by anodic dissolution process taking place at GBs, and might be considered as a driver for softening behavior.

**Summary**

In summary, a combined experimental and atomistic study was used to rationalize potential sources causing the mechanically degraded layer near internal surfaces of corroded grain boundaries detected by nanoindentation. Results suggested that non-equilibrium lattice
vacancies, rather than interstitial hydrogen atoms, generated by intergranular corrosion activity at GB are more susceptible for the GB degradation. The atomic vacancies in the diffusion layer nearby GBs facilitates the dislocation nucleation by decreasing the critical load required for nucleation. It was found that and the degradation level in the diffusion layer next to GBs is controlled by the vacancy concentration, varying with the distance relative to grain boundary according to the diffusion law.

References


CHAPTER 9. CHARACTERIZATION OF SUB-SURFACE MECHANICAL DEGRADATION INDUCED BY INTERGRANULAR CORROSION IN A PIPELINE STEEL

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Denizhan Yavas\textsuperscript{a}, Pratyush Mishra\textsuperscript{c}, Abdullah Alshehri\textsuperscript{b}, Pranav Shrotriya\textsuperscript{b}, Kurt R. Hebert\textsuperscript{c}, Ashraf F. Bastawros\textsuperscript{a}

\textsuperscript{a}Department of Aerospace Engineering, Iowa State University, Ames, IA, 50011, United States
\textsuperscript{b}Department of Mechanical Engineering, Iowa State University, Ames, IA, 50011, United States
\textsuperscript{c}Department of Chemical and Biological Engineering, Iowa State University, Ames, IA, 50011, United States

Abstract

This study examines sub-surface mechanical degradation of an X70 pipeline steel generated by high-pH intergranular corrosion (IGC) in sodium bicarbonate solution. Scanning electron microscope examination of the angle-polish corrosion surface was performed to examine the material evolution within the IGC affected near surface of material. Quasi-static and dynamic nanoindentation were utilized to characterize mechanical properties of top corrosion product and IGC-affected layers, respectively. The indentation
modulus profiles as a function of penetration depth obtained from indentations on top surfaces of samples were used to predict the corrosion product thickness by considering the examined corrosion samples as a soft film on a hard substrate. The continuous indentation measurements conducted on the IGC-affected layer exhibited 10% reduction in the indentation hardness, without a noticeable change in the elastic modulus. Additionally, the indentation size effect study showed that the observed reduction in the indentation hardness can arise from the reduction of the lattice resistance (Peierls-Nabarro stress). It was suggested that the observed preferential dissolution of Si atoms can leave behind clusters of atomic vacancies, and thereby weaken the lattice within the IGC-affected sub-surface. The present findings are anticipated to provide new insights for better mechanical understanding of intergranular corrosion and thereby intergranular stress corrosion cracking.

Introduction

Stress corrosion cracking (SCC) refers to the failure by cracking of metals under combined effect of a corrosive environment and tensile stress. SCC affects a wide range of high strength alloys [1]. A critical aspect of SCC is the brittle failure of high-strength alloys, and the associated reduction of the fracture toughness. There is widespread debate about the mechanism of SCC, including the contributions of mechanical vs. chemical processes in the initial damage percolation, leading to a macroscopic crack growth and the associated role of hydrogen embrittlement. Several mechanisms suggest that brittle cracking is produced by localized plastic deformation activities caused by dislocation emission and motion accompanying localized corrosion at the crack tip [1-4]. The pH plays a significant role in defining the operative chemo-mechanical mechanisms that leads to SCC in steels. High pH
SCC is attributed to anodic dissolution at the grain boundaries and repeated rupture of passive films that form over the crack tip, and thereby leading to intergranular failure. The near-neutral pH stress corrosion cracks is due to the synergistic effects of stress and hydrogen on anodic dissolution at crack-tip, and thereby leading to transgranular failure [6, 7].

Most of pipeline steels are found to be vulnerable to both intergranular stress corrosion cracking (IGSCC) and intergranular corrosion (IGC) in “high-pH” (i.e. pH 8-10) carbonate-bicarbonate solutions [1]. However, in terms of electrochemistry, it was shown that IGSCC and IGC tends to occur under the same electrochemical conditions, including pH values and range of the active dissolution potentials [6-10]. This is a direct manifestation of strong coupling between IGSCC and IGC, especially in the early stages. Therefore, it is very relevant to understand the IGC-induced mechanical property degradation in order to fully understand the material response to IGSCC. There has been a numerous different mechanisms proposed to understand initiation mechanism of IGSCC, however, that is not completely understood yet. The majority of the proposed models reported a corrosion-induced material property changes localized at GBs [11-18]. For example, the localized plasticity due to enhanced dislocation nucleation and mobility at GBs is frequently attributed to absorption of hydrogen produced by cathodic reduction of water accompanying corrosion [11-13]. Alternatively, hydrogen promoted accumulation of excess vacancies at GBs can reduce the ductility, resulting in formation of brittle layers at GBs [14-18].

The present study focuses on the identification of the sub-surface mechanical property degradation during early stage high-pH IGC of an X70 pipeline steel in sodium bicarbonate solution. Scanning electron microscope (SEM) examination of the angle-polish corrosion surface was used to characterize the IGC evolution morphology within the IGC-
affected subsurface of the material. The quasi-static nanoindentation was used to estimate the top corrosion product thickness. Independently, the thickness was measured by a non-contact optical profilometer. It was found that the modulus-based thickness estimations are in good agreement with those obtained by profilometer for two different exposure times. In addition, dynamic indentation preformed within the IGC-affected sub-surface showed 10% reduction in the indentation hardness, without a noticeable change in the elastic modulus. An indentation size effect study showed that the observed reduction in the indentation hardness can arise from the reduction of the lattice resistance. It was suggested that the observed preferential dissolution of Si atoms can leave behind clusters of atomic vacancies, and thereby weaken the lattice within the IGC-affected sub-surface.

**Experimental Details**

The samples of a high strength low-alloy pipeline steel (API X70) were machined from a pipe wall. The specimens were cut along the long axis of the pipe, with the top surface in the longitudinal-short transverse plane as shown in Figure 9-1(a). The sample dimensions were 1 mm thick, 18 mm long and 18 mm wide. The main alloying elements in X70 are Mn (~1.75 wt. %), Si (~0.45 wt. %), and C (~0.17 wt. %). Figures 1(b-c) depict scanning electron microscopy (SEM) images of the microstructure on the examined plane. The microstructure is mainly composed of ferrite (dark gray shaded) and pearlite (light gray shaded) phases. Grain boundaries are clearly visible with tiny light gray-shaded line-features. The pearlite phase is elongated along the rolling direction, whereas the ferrite grains are found to be equiaxed with average size of about 5-10 μm.
The sample surfaces were polished with 400, 600 and 800-grit sandpaper, followed by cleaning with deionized water and ethanol. Electrochemical experiments were carried out in a three-electrode cell with Pt wire counter electrode and Ag/AgCl reference electrode. All cited potentials are with respect to this reference. The test solution was naturally aerated aqueous 1 M NaHCO$_3$ at room temperature. Solutions were prepared using analytical grade reagents and deionized water (resistivity 18 MΩ-cm). The applied potential was first held at -1.0 V for 5 min to cathodically reduce surface oxide, and then stepped or scanned in the anodic direction. For examination of the corrosion morphology in cross section, samples were polished to reveal planes at orientations either perpendicular to or at a shallow angle from the surface. Corrosion specimens were examined by scanning electron microscopy (SEM, FEI Quanta 250).
Two steps of nanoindentations (1) quasi-static indents using 3D OmniProbe transducer with Berkovich indenter tip; (2) dynamic indents using NanoDMA® III transducer with 90° cube corner indenter tip was performed by a Hysitron TI 950 TriboIndenter. The former was conducted on top surfaces of corrosion samples and used to mechanically characterize the top corrosion product layer, and to predict its thickness. The latter was performed on the polished surfaces of corrosion samples, and used to examine the depth dependent mechanical properties of intergranular corrosion layer. The indentation hardness, \( H \), and elastic modulus, \( E \), were extracted from force-displacement curves using the Oliver-Pharr method [19]. In addition, the thickness of corrosion product layer on corrosion specimens was measured by a non-contact optical profilometer (Zygo NewView 6300).

**Results and Discussions**

**Electrochemical Measurements and Microstructural Characterization**

The potential region of susceptibility to IGC and IGSCC was found to be between -0.6 V and -0.4 V by potential sweep experiments as consistent with the literature [7, 9, 10]. Accordingly, potentiostatic experiments were performed at the intermediate potential of -0.521 V. Figure 9-2(a) shows the anodic dissolution current density transients at this potential for two different exposure times. The current density typically decays to a minimum value after about 3-5 min, then rises up to a peak value 0.45 mA/cm\(^2\). In the early stage of IGC activity prior to the peak current density, the corrosion product consists of scattered circular particles with average diameter of 2-3 \( \mu \)m, as shown in Figure 9-2(b). The 15 min corrosion surface also exhibits a gel-like layer, dark gray-shaded regions between the
scattered corrosion product particles. EDS spectra of the gel-like layer shows higher concentrations of Si compared to the alloy surface or the corrosion particles. This can be perceived as an evidence for selective dissolution of Si at the grain boundaries during the initial chemical attack. After the current maximum, the steel surface was covered by a continuous corrosion product layer, as shown in Figure 9-2(c).

Figure 9-2  (a) the anodic dissolution current density transients at this potential for two different exposure times, (b, c) scanning electron microscope images showing the corroded surface after the 15 min and 2h corrosion exposure, respectively.

The corrosion samples were polished by a very small angle in order to reveal the intergranular corrosion morphology on a plane nearly parallel to the top surface. Figure 9-3 shows SEM images of the 2h corrosion sample. The lower magnification SEM image in Figure 9-3(a) depicts three distinct layers, namely a top corrosion product layer, a near-
surface intergranular corrosion layer, and uncorroded base alloy. It should be noted that the length scale along the vertical direction in the low magnification SEM image is magnified by a factor of about 1000 due to the shallow angle polishing [20]. Figures 9-3(b)-(c) illustrate the higher magnification SEM images of corrosion product layer. The corrosion product layer consists of circular particles few microns in diameter. The observed mud-cracks is attributed to drying process of the top product layer. Figure 9-3(d)-(e) depict higher-magnification SEM view of intergranular corrosion layer at a selected depth within IGC layer. The first observation is that the intergranular corrosion selectively targets the triple junctions between the equiaxed ferrite grains. Second, the corrosion attack opens central voids, which can be viewed as black-shaded crevices in Figure 9-3(d). Third, the corrosion process surrounds the grain cores (white shaded regions) with a product layer corrosion product layer (gray shaded layer around the grain cores).

Figure 9-3 (a) Scanning electron microscope image (SEM) of the angle-polished surface of 2h corrosion sample, revealing three distinct layers, and higher magnification SEM images of the top corrosion product layer (b, c) , and IGC–affected layer (d, e)
Figure 9-4  (a) Higher magnification scanning electron microscope image (SEM) of a triple junction in the IGC affected layer. (b-d) Fe, O, and Si content intensity maps, respectively. (e) EDS spectra of the selected region.

Figure 9-4 shows the EDS analysis of a region around a triple junction within the IGC layer as shown in SEM images in Figure 9-4(a). Figures 9-4(b), (c), and (d) respectively
show Fe, O, and Si content intensity maps for the inspected region. In addition, Figure 9-4(f) shows EDS spectra of the selected regions marked in Figure 9-4(a) as (1) the core of the grain and (2) GB corrosion product layer, as well as the EDS spectra of the top corrosion product layer. As expected, the corrosion product layer surrounding grains core exhibits relatively lower Fe and higher O content, compared to the core of grains. EDS spectra of the top corrosion product layer and GB corrosion product layer were found to be very similar, both revealed that their major constituents are Fe, O and C, suggesting that the film is an iron hydroxy-carbonate as found previously [21]. Surprisingly, GB corrosion product layer depicted relatively augmented silicon content, compared to the core of the grains. This Si-enrichment can be attributed to the selective oxidation of silicon solute atoms during the initiation stage of IGC.

**Corrosion Product Thickness Measurement by Non-contact Interferometry**

A non-contact optical profilometer (Zygo NewView 6300) was also utilized to independently measure the average thickness of the corrosion product layer. The measurements were performed on the edge of the corroded surface relative to the uncorroded base surface, as well as the cleaned surface, where the corrosion product layer was removed by wiping the surface with a swap dippen in a diluted acetic acid solution right after the corrosion experiments. Figure 9-5(a) illustrates the 3-D surface profile for 2h corrosion surface, where three distinct regions: (1) a corrosion product layer, (2) an uncorroded base surface and (3) a cleaned surface can be identified. In order to show height transitions across these different regions, Figures 9-6(a) and (b) illustrate the line profile along lines A and B marked in Figure 9-5(a), respectively. First, the height profile along the line A does not show a significant height difference between the uncorroded surface and the cleaned surface. The
profile along the line A on the corrosion product layer exhibits high surface roughness due to the semi-spherical shape of the corrosion product particles. However, the height profile on the cleaned surface reveals relatively smaller roughness with minimum and maximum extreme points. The former is attributed to GB fissures (voids) shown in Figure 9-3(d). The latter can be associated with remnants of corrosion product particles due to improper cleaning process. Second, the height profile along the line B shows an average thickness of the corrosion product layer $t = 3.5\mu m$. Figure 9-5(b) illustrates the 3-D surface profile for 1h corrosion surface. Figure 9-6(c) also presents the profilometer along the line C shown in Figure 9-5(b). An average thickness of the corrosion product layer was measured to be $t = 1.8\mu m$.

![Figure 9-5 3D surface profiles measured by non-contact optical profilometer for (a) 2h and (b) 1h corrosion samples, showing the corrosion product layer at edges of exposure regions, with a field of view of 550 x 550\(\mu m^2\).](image)

The corrosion product layer thickness measured by non-contact optical profilometer increased from $t = 1.8\mu m$ to $t = 3.5\mu m$ with increase of the exposure time from 1h to 2h.
The corresponding ratios of thickness to charge density were $2.1 \times 10^{-4}$ at 1h and $2.0 \times 10^{-4}$ cm$^3$/C at 2h. These values can be compared to the increases of corrosion product thickness with charge density associated with the formation of the possible product layer constituents. The corrosion product formed in bicarbonate solutions is an iron hydroxycarbonate, which at -0.521 V may contain both and Fe(II) and Fe(III) compounds [7, 21]. The thickness-charge density ratio for compact product layers based on the molar volumes of Fe(OH)$_2$, FeCO$_3$ and Fe(OH)$_3$ are respectively $1.4 \times 10^{-4}$, $1.5 \times 10^{-4}$ and $9.5 \times 10^{-5}$ cm$^3$/C. The porosity of the product layer is consistent with the somewhat larger ratios found experimentally.

![Figure 9-6](image)

Figure 9-6  The height profiles along the lines A, B, and C marked on (a, b).
Mechanical Characterization of Corrosion Product Layer

The mechanical properties of the top corrosion product layer deposited on the sample surface were measured by high load quasi-static indentations. Two corrosion samples with different exposure times (1h and 2h) and a reference sample (no corrosion) were examined. A sequence of nanoindentations were performed on each sample with progressive increase of the peak load between 1 and 250 mN. A trapezoidal loading profile, consisting of a 5 s linear loading, 2 s hold at the peak load, and 5 s linear unload, was applied. The maximum depth of indentation was recorded to be about 4μm for 2h corrosion sample. Figure 9-7(a) shows representative sets of indentation load-depth curves for the examined cases. The reference sample clearly exhibits a stiffer response during loading, compared to the corrosion samples. At relatively shallower indentation depths ($h < 1.5 \mu m$), the corrosion samples show a similar compliant response. Upon further penetration, a stiffening commences for both of the corrosion samples at different characteristic indentation depths. This characteristic penetration depth was observed to be about 1.5 μm and 2.5 μm for 1h and 2h corrosion samples, respectively. The observed stiffening can be attributed to a transition from the soft corrosion product layer to bulk base material.

Figure 9-7(b) shows the measured indentation modulus $E$ as a function of depth, along with the prediction curves by Eq. (1), for the examined three cases. For the reference sample, $E$ was measured to be about 190 GPa and independent of the indentation depth. However, a noticeable drop on $E$ can be seen for the corrosion samples with formation of top corrosion product layer. At the shallower indentation depths ($h < 0.5 \mu m$), the average $E$ is about 20% of that of base material ($E \approx 40 GPa$) with a large scatter. Such scatter can be
attributed to presence of surface roughness arising from non-uniform formation of the corrosion product layer [22].

Figure 9-7 (a) A representative set of indentation load-depth curves for the base (no corrosion), 1h and 2h corrosion samples corroded samples, (b) Indentation modulus as a function of penetration depth for the examined cases.
It should also be noted that the measurements were carried out in the dry state. It remains to be seen if the hydroxylated state might exhibit the same stiffness, as such layer may contribute to the balance of the residual stresses developed during the corrosion process. With increasing penetration depths, the indentation modulus tends to rise up and reach to the level of base modulus. However, the observed transition between the corrosion product and base moduli occurs more rapidly for 1h corrosion sample compared to 2h corrosion sample. This suggests that 2h corrosion sample has relatively thicker corrosion product layer.

**Corrosion Product Thickness Prediction by Nanoindentation**

The examined material system can be perceived as a soft film (corrosion product layer consisting of iron hydroxide and carbonate) on a hard substrate (X70 steel, and thereby the measured indentation modulus profiles as penetration depth can be utilized to estimate thickness of corrosion product for two different exposure time. There has been numerous study related to determination of intrinsic mechanical properties of thin films from indentation data [23-27]. In the present study, the method proposed by Doerner and Nix [23] and modified by King [24] was used to estimate the corrosion product thickness from the measured indentation modulus data. Their method models the film and substrate as two spring, and assumes a linear transition from film to substrate as

\[
\frac{1}{E} = \frac{1}{E_f} + \left( \frac{1}{E_s} - \frac{1}{E_f} \right) e^{-a(t)}
\]

where the subscripts \( f \) and \( s \) refer to the film and substrate, respectively. \( t \) is the film thickness, and \( a \) is the contact radius, which can be estimated by knowing the contact area \( A \) in terms of indentation depth, \( h \). For the utilized Berkovich indenter tip, the contact area
function was calculated to be a second order polynomial form as \( A = 24.5h^2 + 13814h \) by a number of indentations performed on the standard fused quartz sample. Lastly, \( \alpha \) is an empirically determined constant.

For the known substrate and film modulus, which were independently measured on the cross section of the sample to be \( E_s = 200 GPa \) and \( E_f = 29 GPa \), and \( \alpha = 0.17 \), the film thicknesses were predicted by least squares fitting of the measured data for each data set. The film thickness was estimated to be \( t = 1.6 \mu m \) and \( t = 3.4 \mu m \) for 1h and 2h corrosion samples, respectively. The corresponding curves fitted by Equation (1) are presented in Figure 9-7(b). They provide sufficiently match with the experimental data. The large scatter in larger penetration depths can be associated with the fracture of the brittle corrosion product film. The non-contact profilometer thickness measurements were found to be consistent with the thickness prediction by nanoindentation modulus profiles.

**Characterization of Intergranular Corrosion Layer by Dynamic Nanoindentation**

The dynamic nanoindentation measurements were conducted on the angle polished surfaces of corrosion samples (Figure 9-3) to obtain the continuous measurement of indentation modulus and hardness. A regular trapezoidal loading profile in conjunction with an oscillating sinusoidal component in the loading stage was applied to measure the depth dependent mechanical properties. The amplitude of the oscillating force component was varied to be 5% of the quasi-static load with a fixed 220Hz frequency. The nanoindentations were performed on the grain cores within the intergranular corrosion layer and base layer as the baseline measurement. In addition, the top corrosion particles were characterized by dynamic nanoindentations.
Figure 9-8 The variation of the continuously measured indentation (a) modulus and (b) hardness as a function of penetration depth for the examined layers. The inserts depict atomic force microscopy surface scans of a group of indent imprints in the IGC and CP layers.
Figure 9-8 depicts the variation of the continuously measured indentation modulus and hardness as a function of penetration depth. The measurements were averaged over 10 grains, and presented with the error bars representing the standard deviation (color-shaded areas over the data). Within the experimental error, there is not a noticeable difference in the average modulus of the grains in the IGC compared to baseline measurements. $E$ was measured to be about $E = 190 \pm 10 \text{GPa}$ with a few percent variation for the both in IGC and base layers. However, the average $E$ was measured to be $E = 29 \pm 5 \text{GPa}$ with an increasing variation for deeper into the corrosion particle. The insert images in Figure 9-8(a) shows the atomic force microscopy surface scans of a group of indent imprints in the IGC and CP layers. The indents in the IGC layer exhibited significant level of pile-up, whereas no pile-up was observed for the indents in the CP particles.

The hardness measurement of different material layers exhibited many unique features. First, H in the base and IGC layers revealed a continuous decay until reaching a steady state level. Such phenomenon is a direct manifestation of indentation size effect (ISE) [28]. It should be noted that the observed ISE was not an artificial effect of material pile-up observed for the indents on both the IGC and base layers. Normally, the indentation pile-up leads to over estimation of hardness [29], and thereby it can cause an increasing hardness profile with increasing penetration depth. However, the measurements showed a similar ISE trend with that observed for polycrystalline materials. Therefore, the observed ISE can still be perceived to be the true material response, with an insignificant bias arising from the indentation pile-up. Second, the average H profile of IGC layer is consistently lower than that of the base layer throughout the initial decay. Note that, the indentation pile-up height of the indents in the IGC layer was found to be in the same level of that in the base layer.
Therefore, the observed reduction in hardness profile is not associated with errors in the contact area estimation. Evaluating Figure 9-8(b), at shallower penetration depths (\( h < 200\text{nm} \)), the difference in H levels is about 15% of the baseline, whereas, it becomes about 10% of that of the baseline at the steady state level (\( h > 600\text{nm} \)). Accordingly, the average hardness of IGC and base layer were measured to be \( H = 2.95 \pm 0.10\text{GPa} \) and \( H = 3.22 \pm 0.20\text{GPa} \), respectively, at the steady state level. Interestingly, the IGC activity caused a significant drop in the indentation H, without a noticeable change in the measured E. On the other hand, the average H of the corrosion product particle was measured to be \( H = 1.5 \pm 0.2\text{GPa} \), with an insignificant depth dependent behavior.

**Vacancy-induced Weakening of Lattice Resistance by Intergranular Corrosion**

An indentation size effect (ISE) study was performed in order to examine the effect of intergranular corrosion activity on the material plasticity of the grains in the IGC layer. The ISE model for polycrystalline materials proposed by Nix and Gao (thereafter referred as NG model) [28] incorporating the concept of geometrically necessary dislocations (GND) was used to analyze the indentation data. In their model, the depth dependent variation of the indentation hardness is cast in the following characteristic form,

\[
\left( \frac{H}{H_0} \right)^2 = 1 + \frac{h^*}{h}
\]

(2)

where \( H_0 \) is the hardness when the infinite depth becomes infinitely large and \( h^* \) is a characteristic length that depends on the indenter geometry, shear modulus, and \( H_0 \). Incorporating the concept of GND [28], and Taylor dislocation model [30], and Tabor’s
approximation [31], NG model presumes \( H_0 \) as the hardness arising from the statistically stored dislocations alone, and casts into the following form,

\[
H_0 = 3\sqrt{3}\beta\mu b\sqrt{\rho_s}
\]  

(3)

where \( \beta \) is an empirical material constant, \( \mu \) is the shear modulus, \( b \) is the Burgers vector, and \( \rho_s \) is the density of statistically stored dislocations.

Figure 9-9  The square of the measured hardness as a function of reciprocal of the penetration depth for the selected data sets, along with the NG model linear fitting curves for the different material constants.

Two representative hardness data set for the indents in the IGC and base layers were selected to examine the effect of IGC on the depth dependent hardness profiles. The form of
Equation (2) suggests that $H^2$ should be plotted against $1/h$, so that the Nix-Gao model provides a linear correlation, where the interception and slope of the curve are associated with $H_0$ and $h^*$, respectively. Figure 9-9 depicts the square of the measured hardness as a function of reciprocal of the penetration depth for the selected data sets, along with the NG model linear fitting curves with different sets of $(H_0, h^*)$. For the initial portion of the data, $0.0013 \text{ nm}^{-1} < 1/h < 0.0055 \text{ nm}^{-1}$ $(180 \text{ nm} < h < 750 \text{ nm})$, Nix-Gao model presents a good agreement with the measured data. Thereafter, for the smaller penetration depths $1/h > 0.0055 \text{ nm}^{-1}$ $(h < 180 \text{ nm})$, the data exhibits a deviation from the linear behavior, which was attributed to uncertainties in the contact area prediction [28]. Similarly, Feng and Nix showed that N-G model overestimates the indentation hardness of magnesium-oxide for small indentation depth less 200nm [32]. NG model assumes all GNDs are confined in the plastic zone, which is a hemisphere with a radius of a underneath the indenter tip. However, for the small penetration depths, the radius of the process zone is expected to be larger than a. Therefore, the observed deviation arises from the overestimation of the GND density [32, 33].

The NG model predicted $H_0 = 2.71 \text{ GPa}$, $h^* = 261 \text{ nm}$ for the base grain, whereas $H_0 = 2.45 \text{ GPa}$, $h^* = 234 \text{ nm}$ for the grain in the IGC layer. These measurements showed about 10% reduction in $H_0$. According to Equation (3), the observed reduction in $H_0$ has to be compensated by a probable reduction of $b$ and/or $\rho_s$ and/or $\mu$. However, none of these material constants are anticipated to be altered by the IGC activity. Burgers vector $b$ is associated with the lattice constant, and projected to be the same for both measurements. Similarly, the same $\rho_s$ was anticipated for material layers. It was also shown that the elastic
modulus (proportional to $\mu$) is not changed by the IGC. Accordingly, Equation (3) was found to be insufficient to explain the observed reduction in $H_0$. However, for simplicity, the NG model neglects one important term in Equation (3), which is the contribution of the lattice friction stress on $H_0$. The lattice friction stress term in Taylor’s dislocation model [30] represents the intrinsic lattice resistance, and can be perceived as Peierls–Naborro stress. It was shown that the contribution of lattice friction on the nanoindentation hardness is negligibly small for FCC metals, whereas very significant in BCC metals [34, 35]. Accordingly, considering the hardness arising from lattice resistance $H_{p-N}$, then Equation (3) can be modified as follows,

$$H_0 = H_{p-N} + 3\sqrt{3}a\mu b\sqrt{\rho},$$

(4)

Therefore, the reduction of $H_0$ can be arising from the lower lattice resistance (or Peierls–Naborro stress) due to IGC process. The observed weakening of the lattice resistance can be attributed to the non-equilibrium lattice vacancies generated in the IGC layer due to anodic dissolution process. The preferential dissolution of Si atoms can leave behind clusters of atomic vacancies, and thereby weaken the lattice within the IGC layer. Figure 9-4 provides an important evidence for the selective oxidation of silicon solute atoms. In order to obtain further evidence for the IGC-generated non-equilibrium vacancies, Figure 10 shows SEM images of the surface of the 2h corroded sample after removal of the top corrosion product layer by the diluted acetic acid solution. The grains and GB grooves can be identified in Figs. 10 (a) and 10(c). Note that the surface shows different roughness over the core of the grains and GB grooves. The high magnification of SEM images of the marked regions in Fig. 9-10(a) and (b) are provided in Fig. 9-10(c) and (d). There are many nano-dimples or cluster of nano-dimples, which can be perceived as traces of the high concentration of vacancies.
clusters on the wall of GB grooves. It can be suggested that atomic vacancy concentration varies inside the grain with the distance relative to the GB.

Figure 9-10 SEM images of the surface of the 2h corrosion sample after removal of the top corrosion product layer by the diluted acetic acid solution, highlighting nano-dimples or cluster of nano-dimples, which can be perceived as traces of the high concentration vacancies cluster on the wall of GB grooves.

Similarly, it was previously shown that the anodic dissolution can results in atomic vacancies that diffuse into the steel, and have been considered as a driver for softening behavior [17, 18]. Guo et. al. suggested that electrochemical dissolution-induced degradation of iron might be plausibly explained by the generation of non-equilibrium vacancies in the subsurface layer, possibly associated with oxidation of reactive solute atoms [17]. Despite
uncertainty about the precise degradation mechanism, the observed IGC-generated lattice resistance weakening is mechanistically relevant to stress corrosion cracking, as it occurs in the potential and pH range of highest susceptibility of X70 steel to IGSCC.

**Conclusion**

The present study focuses on the identification of the sub-surface mechanical property degradation during early stage high-pH IGC of an X70 pipeline steel in sodium bicarbonate solution. Scanning electron microscope (SEM) examination of the angle-polish corrosion surface was used to characterize the IGC evolution morphology within the IGC-affected subsurface of the material. The quasi-static nanoindentation was used to estimate the top corrosion product thickness. Independently, the thickness was measured by a non-contact optical profilometer. It was found that the modulus-based thickness estimations are in good agreement with those obtained by profilometer for two different exposure times. In addition, dynamic indentation preformed within the IGC-affected sub-surface showed 10% reduction in the indentation hardness, without a noticeable change in the elastic modulus. An indentation size effect study showed that the observed reduction in the indentation hardness can arise from the reduction of the lattice resistance. It was suggested that the observed preferential dissolution of Si atoms can leave behind clusters of atomic vacancies, and thereby weaken the lattice within the IGC-affected sub-surface.
References

1. Y.F. Cheng, Stress Corrosion Cracking of Pipelines, Wiley 2013


CHAPTER 10. INTEGRATIVE SUMMARY AND FUTURE WORK

This thesis presented some physical and mechanical understanding of interfacial degradation mechanisms in two different problem sets. The first part examined the contamination-induced interfacial degradation mechanisms in polymer matrix composites. The second part studied the early stage degradation of microstructure and mechanical properties in a pipeline steel undergoing high-pH intergranular corrosion in sodium bicarbonate solution. The findings provided some metrics for the physical and mechanical changes associated with these degradation mechanisms, which can be employed to provide the bases for further development of new nondestructive evaluation techniques.

In Chapter 2, a correlation between the residual interfacial fracture toughness and the nanoindentation hardness was presented for adhesively bonded composite joints. While the present scaling was verified for a common adhesive-adherend material system, with additional examination of other systems, the proposed scaling law might facilitate the utilization of the perceived non-destructively evaluated indentation hardness to serve as an indicator for the bond line quality.

In Chapter 3, the effect of environmental contamination level on the mode-I failure and fracture surface evolution of adhesive joints was studied. The study revealed:

(1) An Arrhenius-type correlation between interface toughness and contaminant concentration, with potential to predict the bond line toughness deterioration level.

(2) A change in the fracture surface morphology (ductile-to-brittle failure mode transition) with increasing contamination level, driven by the limited plastic (or in-elastic) deformation of the adhesive layer.
(3) Two interdependent interfacial degradation mechanisms: (i) weakening the interfacial bonding strength, and thereby reducing the interfacial toughness, and (ii) shielding the plastic energy dissipation within the adhesive layer, and leading to a reduction in the overall effective bond line toughness.

In Chapter 4, a correlation between the residual interfacial fracture toughness and the contaminant concentration was presented using the principals of interfacial fracture mechanics and modified Gibbs adsorption equation. The present correlation might provide the basis for non-destructive evaluation of bond line integrity by assessing the adsorbed species level using infrared spectroscopy.

In Chapter 5, a linear correlation between the interfacial toughness and the resulting fracture surface roughness was presented for a polymer-based interfaces using statistical fracture surface analysis. The study showed that:

(1) the roughness exponent of the self-affinity is independent of the interfacial toughness level;

(2) the cut-off length scale of the self-affinity exhibits a linear correlation with the varying interfacial toughness level.

The observed correlation was found to be dictated by the process zone size in front of the crack tip, which is controlled by the intrinsic interfacial toughness. The present correlation shows potential for the utilization of the statistical characterization of the fracture surfaces to estimate the residual interfacial toughness.

In Chapter 6, morphology and mechanical stress evolution during high-pH intergranular corrosion of X70 pipeline steel in sodium bicarbonate solution was presented. It was found that IGC produces crevices at grain boundary triple junctions and triangular
wedges of corrosion product around the triple junctions. Mechanical stress evolution during corrosion was monitored using in situ stress measurements and related to internal oxidation within the IGC layer. Evidence was also presented for selective oxidation of silicon solute at grain boundaries during the early stages of intergranular attack.

In Chapter 7, locally resolved ex-situ nanoindentation measurements at corroded grain boundaries in X70 pipeline steel were presented. The study revealed evidence for degradation of hardness near grain boundaries. These are apparently the first observations of local corrosion-induced softening of grain boundaries under conditions associated with high SCC susceptibility.

In Chapter 8, a combined experimental and atomistic computational study of the grain boundary degradation in a pipeline was presented. The study showed that:

(1) non-equilibrium vacancies, rather than interstitial hydrogen-atoms, generated by intergranular corrosion promotes dislocation nucleation, which in turn, results in grain boundary degradation;

(2) the degradation level in the vicinity of grain boundaries is controlled by the vacancy concentration, varying with the relative distance to grain boundaries according to Fickian diffusion law.

In Chapter 9, sub-surface mechanical degradation of an X70 pipeline steel generated by high-pH intergranular corrosion in sodium bicarbonate solution. The continuous indentation measurements conducted within the IGC-affected layer exhibited 10% reduction in the indentation hardness, without a noticeable change in the indentation modulus. The indentation size effect study suggested that the observed reduction in the indentation hardness can arise from the reduction of the lattice resistance (Peierls-Nabarro stress). The
observed preferential dissolution of Si atoms can generate clusters of atomic vacancies, which leads to vacancy-induced weakening the lattice within the IGC-affected sub-surface. The present findings are anticipated to provide new insights for better mechanical understanding of intergranular corrosion and intergranular stress corrosion cracking.

In the future, the proposed correlations in the first part of the thesis (Chapters 2-5) can be applied to other adhesive/adherend material systems such as polymer/metal, polymer/polymer etc. Alternatively, the effect of other environmental effects such as moisture, temperature on the observed trends can be studied for the same material system. A similar study can be performed for pure mode-II or mixed-mode fracture and the present correlations can be extended for a range of mode-mixities. While that has not been presented here, an interest dependence on the mode-mixity has been discovered and will be published later. In addition, it might be very interesting to test the proposed correlations with real field data and show the viability of the recommended non-destructive testing schemes. This may facilitate development of new non-destructive evaluation techniques based on the proposed schemes for the early detection of interfacial damage, and assessment of the remaining safe service life of the adhesively bonded composite structures in aerospace industry.

For the second part (Chapters 6-9), the present morphological observations and degradation mechanisms address IGC, because the samples were free of tensile stress during the electrochemical experiments. Although IGC is very relevant to IGSCC, a similar study has to be carried out under tensile stress in order to confirm the observed trends for IGSCC. A new experimental setup has been designed to produce IGSCC samples with varying tensile stress level and time of exposure, even though it is not presented in this thesis. In addition, the proposed nanoindentation testing scheme in the vicinity of grain boundaries can be
performed in-situ, although there are several limitations with in-situ indentation during electrochemical exposure. The atomistic computational models were successfully used to understand the vacancy-induced softening in the vicinity of grain boundaries. The observed grain boundary softening is not a triggering mechanism for IGSCC initiation and evolution, it is rather a consequence of enhanced dislocation mobility by non-equilibrium vacancies. However, IGSCC evolution can be associated with a weaker grain boundary (with reduced cohesive energy) arising from excess vacancy concentration. Therefore, a detailed atomistic computational analysis including a grain boundary can also be carried out to model vacancy-induced grain boundary weakening, in addition to the vacancy-induced grain boundary softening.