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Fretting Wear Mechanisms in A216 Plain Carbon Steel

By

Alyssa Anne Maich

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Engineering – Materials Science and Engineering in the Graduate Division of the University of California, Berkeley

Committee in charge:
Professor Ronald Gronsky, Co-Chair
Professor Kyriakos Komvopoulos, Co-Chair
Professor Fiona Doyle
Professor Lisa Pruitt

Spring 2016
Fretting Wear Mechanisms in A216 Plain Carbon Steel

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By

Alyssa Anne Maich
The subsurface and surface microstructures during pin-on-disk fretting wear of A216 steel disks under various loading conditions and times are investigated. The corresponding pins are fabricated from 410 stainless steel to simulate in-service conditions found in such engineering components as the Siemens W501FD engine row-2 diaphragm of a Siemens turbine engine, which is known to be prone to failure by fretting wear. Loading conditions range from 2N to 15N and times from 1 hour to a maximum of 69 hours, when steady state is confirmed. Wear track depth is quantitatively determined by optical profilometry, and found to range from 3 to 11 microns dependent upon load. Wear depth increases from 2N to 10N load, but decreases when increased to 15N load, due to heavier transfer of pin material to disk, as can be seen by EDS images of chromium transfer on A216 disk. Microstructures are evaluated by transmission electron microscopy of samples prepared by focused ion beam machining to pinpoint wear tracks and expose them in cross-section. EDS is used, in conjunction with TEM, to elucidate primary wear mechanisms at each stage of fretting wear. Microstructures in the subsurface of wear tracks are found to be heavily dislocated and layered, features that vary with both applied load and time. The microstructure eventually evolves into stable dislocation cells with cell walls aligned parallel to the surface. Penetration depth of the damaged layers increases with applied load, associated with a non-uniform maximum shear stress distribution that varies with depth. Primary oxide appears to evolve from Fe₂O₃ to Fe₃O₄, with increasing fretting time, leading to a uniform oxide on the surface of the A216 disk. Oxidation rate may be increased with the evolution of this subsurface dislocation cell structure. It is concluded that fretting wear failure is likely associated with a synergy between oxidative wear and crack initiation and propagation along dislocation cell walls under high strain accumulation at sufficiently high loads or sufficiently long times.
For my son, Anthony Jase.
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<td>ASTM</td>
<td>American Society for Testing of Materials</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscope/Microscopy</td>
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<tr>
<td>BCC</td>
<td>Body-Centered Cubic</td>
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<tr>
<td>FCC</td>
<td>Face-Centered Cubic</td>
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<tr>
<td>BCT</td>
<td>Body-Centered Tetragonal</td>
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<td>HCP</td>
<td>Hexagonal Close-Packed</td>
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<td>CCT</td>
<td>Continuous Cooling Transformation</td>
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<td>EDS</td>
<td>Energy Dispersive Spectrometry/ Spectroscopy</td>
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<td>TEM</td>
<td>Transmission Electron Microscope/Microscopy</td>
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<tr>
<td>SAD</td>
<td>Selected Area Diffraction</td>
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<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
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<td>PSB</td>
<td>Persistent Slip Band</td>
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<td>k</td>
<td>Archard’s wear coefficient</td>
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<td>V</td>
<td>Wear volume</td>
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<tr>
<td>x</td>
<td>Sliding distance</td>
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<td>L</td>
<td>Normal/Applied load</td>
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<tr>
<td>H</td>
<td>Hardness</td>
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<tr>
<td>(p_m)</td>
<td>Yield stress</td>
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<tr>
<td>Z</td>
<td>Holm’s wear coefficient</td>
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<tr>
<td>(k_{ab})</td>
<td>Abrasive wear coefficient</td>
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<tr>
<td>(\tau_R)</td>
<td>Resolved shear stress</td>
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<td>(\gamma)</td>
<td>Shear strain</td>
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Acknowledgements

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Chapter 1

Background

1.1 WEAR

Wear is formally defined by the American Society for Testing of Materials [ASTM G40-13] as the alteration of a solid surface by progressive loss or progressive displacement of material due to relative motion between that surface and another contacting surface. Therefore, wear most often involves the removal of material from one or both contacting surfaces in relative motion. Figure 1 depicts a generic wear system, which conventionally has three or four parts: (i) a wear couple (body and counter-body), (ii) an interfacial medium (such as a lubricant), and (iii) a surrounding medium (environment). Such a system can be analyzed in terms of operating variables vs. wear characteristics. The operating variables include the applied load(s), time, relative (sliding) velocity, and temperature. Previous work, conducted by Welsh et al. [1] on plain-carbon steels, clearly shows that a small change in operating variables, such as an increase in load from 100 to 200 g, can have a significant effect on wear rate (by two orders of magnitude). Because these small changes can have such a significant effect on the wear rate, it is important to study a material’s wear behavior under different operating conditions.

![Figure 1.1 Representative tribological system](image)

Comparing wear states mandates careful analysis of appropriate data. In general, wear comprises two stages: running-in and steady-state. The running-in stage is defined as the initial transient sliding process occurring in newly established contacts, often accompanied by transients in coefficient of friction, wear rate, or both, which may be uncharacteristic of the long-term behavior of a given tribological system [ASTM G40-13]. The simultaneous occurrence of many phenomena during the running-in stage, such as work hardening, surface chemistry changes, plastic deformation of asperities, and stress/temperature-induced phase transformations, make it especially difficult to comparatively examine the initial wear performance of a system. Steady-
state wear is associated with the long-term behavior of a tribological system. Because conditions have stabilized in steady-state stage of wear, a comparative analysis can be performed. To thoroughly understand the wear process, an in depth analysis of the wear mechanisms and material properties during both running-in and steady-state stages is essential. In fretting wear, the steady-state stage is identified as that at which the hysteresis of the friction force versus relative displacement of the surfaces does not change with fretting cycles.

Previous investigators attempted to classify wear based on loading of the system in question.\textsuperscript{[3,4,5,6]} Loading of two mating surfaces can be very complex, since the two surfaces are generally not in perfect contact due to time-dependent undulations (asperities) on the interacting surfaces, resulting in a time-dependent pressure distribution at the surface. Consequently, rather than analyzing wear characteristics with respect to pressure, it might be more illustrative to analyze the slip regime induced by a particular load and sliding distance.

There are three different regimes in small-amplitude reciprocating sliding: no slip (stick), slip, and mixed (stick-slip) regimes.\textsuperscript{[7]} To reduce relative motion at the interface, the tangential (friction) force must overcome the resisting force within the elasticity limits of the bulk material.\textsuperscript{[6]} The typical contact pressure distribution (for a ball, cylinder, or ellipsoid) has a peak pressure at the center of the contact and decreases non-linearly outward the contact edge. This favors stiction at the center of the contact and slip within an annulus between the stick region and the contact edge.\textsuperscript{[6]} As the contact load increases, the slip annulus decreases until eventually the stick regime fully occupies the contact region and relative motion between the two solid bodies vanishes. It is therefore important to determine the dominant regime during fretting wear. This can be accomplished by examining the characteristic wear features of each wear process. Complete determination of the wear regime requires a comprehensive analysis of the friction force vs. displacement hysteresis response of each experiment.

Among the various standardized wear testing methods used to quantify sliding wear of materials, such as block-on-ring, crossed cylinder-on-cylinder, and pin-on-disk (POD),\textsuperscript{[8]} the last of these is often favored because of its simplicity; therefore, the POD test [ASTM G99] was chosen for this investigation. The POD fretting machine used in this work uses as input the load, oscillation frequency, reciprocating distance (time and velocity), and temperature, although temperature changes were not considered in this study.
The main objective of this study was to investigate the fretting wear performance of plane-carbon steel disks in reciprocating sliding with stainless-steel pins under loads resulting in contact pressures typical of those encountered in the Siemens W501FD engine row-2 diaphragm, seen in Figure 1.2. All of the experiments were carried out in ambient air. The high temperatures reached during engine operation cannot be replicated with the current apparatus. It is possible that in the long-term application diffusion processes driven by the elevated temperatures could cause microstructure changes and phase transitions. In this dissertation, the focus is on structural changes induced by the fretting process. With a better knowledge of the fretting process obtained from the present investigation, future thermo-mechanical fretting wear experiments that more closely will resemble field conditions could be formulated. The absence of a lubricant film simplified the present tribosystem, although the formation, rupture, and replenishment of an oxide layer during reciprocating sliding could be modeled as a solid lubricant at the pin/disk interface.

### 1.2 WEAR MECHANISMS

Wear may occur by one or more mechanisms depending on various factors, such as applied loads, elastic-plastic material properties, and environmental conditions. The most common wear mechanisms are abrasion, adhesion, contact fatigue, and tribochemical (oxidational, corrosive, etc.) mechanisms. Micrographs of surfaces worn by these mechanisms are shown in Figure 1.3. Abrasion and adhesion are typically modeled using hardness as the controlling material property. Abrasion (Figure 1.3a) yields a scratched, grooved, or rippled surface. Adhesion

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Figure 1.2 Longitudinal cross-section of the W501F Siemens turbine engine, displaying the location of the Row-2 diaphragm. [9]
(Figure 1.3b) causes back-forth transfer of material between contacting surfaces; this material is then plastically deformed (smeared), appearing as a platelet type configuration. Severe adhesive wear produces scuffing or galling in several surface areas (extensive extrusion of material), material transfer, plastic shearing, and pinholes. Contact fatigue wear (Figure 1.3c) is mainly characterized by the formation and growth of surface cracks, which may also coalesce to create a pitting of material with a generally semi-smooth appearance. In tribochemical (e.g., corrosive) wear (Figure 1.3d), the rubbing process is conducive to the removal (rupture) and replenishment (by a thermally activated process) corrosive surface layer, which, under uncontrolled conditions, can significantly increase the wear rate.

The aforementioned wear mechanisms (summarized in Table 1.1) have one thing in common – the undesirable removal of material from both rubbing surfaces. Most wear processes usually involve a combination of these wear mechanisms (with one, generally, dominating the steady-state wear behavior). Therefore, identifying the dominant wear mechanism(s) is of critical importance in any wear study.
Generally, scanning electron microscope (SEM) images are used to visually distinguish the dominant wear mechanism(s) operating on a surface. The previously discussed wear characteristics are summarized in the table above. Although this is an effective method for identifying surface wear mechanisms, this method of analysis is not conducive to understanding the developing microstructure below the sliding surface. The subsurface microstructure can affect all of the previous wear mechanisms (Table 1.1). For example, microstructure changes may significantly alter the strength (hardness) of the material. If adhesion or abrasion is the prevailing wear mechanism, a change in hardness can greatly affect the wear rate.\[14\] In the case of contact fatigue wear, a change in microstructure (including, but not limited to, rearrangement and creation of dislocations) can have a huge effect on the formation of subsurface fatigue cracks. For systems in which tribochemical reactions are prevalent, a change in microstructure can have an impact on strain-dependent oxidative properties, and can create pathways for oxidation to occur more aggressively.

### 1.2.1 Adhesive Wear

Adhesive wear is due to localized bonding between contacting solid surfaces leading to material transfer between the two surfaces or loss from either surface [ASTM G40–13]. Adhesive wear is the most fundamental of the wear mechanisms. Even in the absence of all other wear mechanisms, adhesive wear can be present between two rubbing surfaces.\[10\]

![ADHESIVE WEAR](image)

Figure 1.4. Illustration of the adhesive wear process.
In adhesive wear, a bond is formed between asperities of the interacting surfaces. If the strength of the adhesive bond is greater than the bond strength in the softer of the two materials, the softer material eventually detaches and transfers to the harder material. The transferred material may become dislodged at a later stage and form a loose wear particle. The initial material detachment and transfer to the opposed surface process is illustrated in Figure 1.4. As rubbing of the two surfaces progresses, the transferred material becomes compacted. An SEM image of this type of wear can be seen in Figure 1.3b.

Archard\textsuperscript{[14]} analyzed the mechanics of multiple asperity contacts with respect to their elastic and plastic deformations and derived the following adhesive wear equation

\[ V = k \frac{L \cdot x}{3H} \quad (1) \]

where \( V \) is the volume of worn off material, \( x \) is the total distance of sliding, \( k \) is termed the adhesive wear coefficient, representing the probability that an asperity junction would lead to forma a wear particle, \( L \) is the applied normal load, and \( H \) is the hardness of the worn material. The adhesive wear coefficient \( k \) typically varies between \( 10^{-8} \) (atomic-scale wear) and \( 10^{-2} \) (severe adhesive wear, commonly known as scuffing), depending on the load, environmental conditions (e.g., in vacuum, in air, contaminated/lubricated) and material properties.

Holm\textsuperscript{[15]} introduced a similar wear equation of adhesive wear, i.e.,

\[ V = Z \frac{L \cdot x}{\sigma_Y} \quad (2) \]

where \( Z \) is the wear coefficient, termed as the probability of removing atomic-size particles or layers becoming loose wear debris, and \( \sigma_Y \) is the yield stress of the worn material. Considering that the yield strength of a material is proportional to its hardness, it be inferred that Equations (1) and (2) are nearly identical.

Significant effort has been devoted to obtaining a relation for the wear coefficient of adhesive wear,\textsuperscript{[16,17,18,19]} which depends on the similarity or affinity of the material surfaces to each other (i.e., metallurgical solubility limit) and environmental conditions (i.e., vacuum, ambient air, poor/good lubricant layer).\textsuperscript{[20]} However, as seen from Equations (1) and (2), a change in hardness may also lead to a significant change in wear rate. Variations in hardness may be associated with changes in surface material properties, such as elastic modulus, yield strength, strain hardening, and toughness. In particular, changes in dislocation density during the progression of adhesive wear can have a significant effect on the hardness of the material being worn off and, consequently, on its wear rate. Therefore, knowledge of the microstructure evolution during surface rubbing is of critical importance.

1.2.2 Abrasive Wear

Abrasive wear is defined as the process in which hard particles trapped at the contact interface and/or hard protuberances (asperities) of a hard surface plowing through the surface of a relatively softer material [ASTM G40–13]. This form of wear is, perhaps, one of the most understood forms of wear. Abrasive wear occurs in a situation where a solid is rubbing against the surface of a countersurface material or trapped particles of equal or greater hardness.
Abrasion mainly involves microscale cutting and plowing processes. The way an asperity slides over a surface determines the nature and intensity of abrasive wear.

There are two basic modes of abrasive wear: two-body and three-body abrasive wear, which are illustrated in Figure 1.5. In two-body abrasive wear, the asperities of the harder surface remove material from the softer surface by a process resembling microscopic cutting. In three-body abrasive wear, small hard particles trapped between sliding surfaces temporarily indent and/or interlock on one of the sliding surfaces and plow through the opposed surface.[10]

Although abrasion differs significantly from adhesion, it is reasonable to consider that the volume of the worn groove is proportional to the contact area of the hard asperity on the soft surface, as proposed by Rabinowicz.[21]

A simple evaluation of abrasive wear produced by a hard surface plowing a groove in a softer surface (wearing away the softer surface), yields a variation of the adhesive wear equation, derived by Archard and Holm, i.e.,

$$V = \tan \theta \frac{L \cdot x}{H}$$

(3)

where $V$ is the wear volume, $L$ is the applied load, $H$ is the hardness of the abraded material, and $\tan \theta$ is the abrasive wear coefficient, where $\theta$ is the slope (sharpness) of the abrading
Equation (3) shows a significant effect of hardness on abrasive wear volume; therefore, also indicating the importance of microstructure changes due to surface rubbing in wear.

1.2.3 Fatigue Wear

Contact fatigue wear is defined as the wear of a solid caused by microcracking induced by cyclic loading of the contacting surfaces [ASTM G40–13]. Alternating mechanical stresses lead to the formation and propagation of fatigue surface and/or subsurface cracks when the material exceeds its fatigue limit. The location of maximum shear stress (i.e., the region where crack initiation is first encountered) depends on the type of contact between the two surfaces. As shown in Figure 1.6, for pure sliding the highest shear stress occurs at the surface, whereas for pure rolling the maximum shear stress arises below the surface, as shown by Hertz theory.\textsuperscript{[10]} These stress distributions indicate that deformation can occur at different surface and subsurface locations, depending on the type of sliding/rolling conditions at the contact interface.

![Figure 1.6. Depth profile of maximum shear stress below the center of contact of a rigid solid of revolution in rolling, sliding, and combined contact with an elastic half-space.\textsuperscript{[10]}](image)

Although contact fatigue wear resembles classical fatigue to some extent, there are a number of differences between the two processes, such as the nonexistence of an endurance limit in contact fatigue, representing infinite life.\textsuperscript{[20]} Because fatigue failure results from crack formation under cyclic loading, the formation of subsurface features that serve as stress concentrators, such as new surfaces, persistent slip bands, and grain interfaces can increase the fatigue wear rate. It is therefore imperative to understand the evolution of the subsurface microstructure due to the accumulation of irreversible deformation due to alternating (cyclic) contact stresses.

1.2.4 Corrosive Wear

Corrosive wear is defined as the wear process in which chemical or electrochemical reactions between a surface and the environment weaken significantly the material surface, leading to the removal of material upon surface rubbing [ASTM G40–13]. Oxidational wear is one of the most
common forms of corrosive wear, because an oxygen-rich environment is a typical environment in which this wear process occurs. Figure 1.7 illustrates the oxidational wear process.

Friction-induced activation of the highly stressed material adjacent to the contact interface may cause it to chemically react with elements in the fluid lubricant or gases from the ambient and form easily shearable reaction products which are eventually removed by the surface rubbing process. For oxidational wear to occur, surface chemical reactivity must be coupled with relative motion of the contacting surfaces. In many instances, oxidative wear is considered to be a “mild-wear” process because the oxide film serves as a solid lubricant, protecting the subsurface metal from a more severe wear mechanism, such as severe adhesive wear (scuffing).

**OXIDATIONAL WEAR**

![Figure 1.7. Illustration of the oxidational wear process.](image)

Oxidational wear may occur by several complex mechanisms. The wear rate of this mechanism is governed by many factors, such as rate of surface oxidation, removal rate of the forming oxide scale(s), normal and shear (friction) surface tractions, geometry of sliding surfaces, whether the whole oxidative surface is removed at once or in part, etc. The oxidation rate depends on many properties, including microstructure. For instance, materials with excess grain boundaries and slip bands enhance diffusion, increasing the oxidation rate of the material. The oxidation rate depends on electronic differences, stress/strain in the material, and thickness of oxide scale. The spallation of the oxide scale (film) may result from increase in strain at the metal-oxide interface. Strain can vary with type of oxide formed (change in atomic misfit and thermal expansion properties), changes in dislocation density in the metal (varying hardness and so changing material compressibility), and thickness of oxide film, which may vary with oxidation rate. A change in hardness of the oxide film oxide forming during surface rubbing and wear can also change the removal rate of the oxide. Consequently, a thorough understanding of the evolution of the subsurface microstructure is necessary to understand the progression of wear with time of surface sliding.
1.3 FRETTING WEAR:

Fretting wear is defined as the wear process encountered in small amplitude (typically 20–200 µm) oscillatory contact of two solid bodies [ASTM G40–13]. Although fretting wear and reciprocal wear can be defined as the same for very short reciprocal distances, there are a few notable distinctions between the two. In fretting wear, the volumetric wear rate increases with increasing stroke amplitude (under constant loading conditions), whereas in reciprocating wear, the volumetric wear rate remains constant, even if the oscillation amplitude is changed,\[^8\] as shown in Figure 1.8.

Fretting wear is sometimes referred to as fretting fatigue. This is mainly for oscillatory contacts predominantly failing by contact fatigue cracking. In fretting fatigue cracks can grow from the surface into the bulk of the material, or below the surface and parallel in the direction of reciprocating sliding for significant time of the fatigue life, before they eventually shear off to the surface and/or intersect with other cracks to cause material to be peeled off — a process collectively known as delamination.\[^{27}\]

![Figure 1.8. Effect of oscillation amplitude (slip distance) on wear volume.][28]

Fretting wear occurs for slip amplitudes below 200–250 µm, where the wear rate (slope) increases with slip amplitude.

Compared to other wear mechanisms, fretting wear has been relatively less studied and not fully understood, despite the fact that this type of wear has been found to be responsible for the catastrophic failure in numerous applications, including industrial machinery, turbine engine parts, MEMS devices, computer boards, microrelays, microswitches, and other other engineering components where a source of vibration is present.\[^{29, 30, 31, 32, 33}\] Fretting wear can increase the clearance between adjacent components in applications where tight tolerances are critical to effective operation (e.g., piston/cylinder interface) and also cause jamming when wear debris is strongly held at the contact interface (e.g., journal bearings).\[^{34}\]
Plastic strains induced during sliding contact produce subsurface damage near the surface, which can be significantly different from the bulk. Fretting wear may also have an “environmental” component, influenced by several factors, such as temperature, humidity, and others.\[35, 36, 37, 38, 39\] Despite of many fretting wear studies of various steels, the mechanisms controlling fretting wear are still not well understood. In most investigations of fretting wear the focus has been on the damaged surface; however, subsurface damage must be considered in conjunction with surface damage to elucidate the mechanisms involved in this type of wear.

Standard material testing usually assesses elastic and plastic bulk properties of the contact pair. However, subsurface imaging studies performed for this dissertation reveal changes in second phase morphologies and severe plastic strain accumulation under the contact area. Very little is known about the correlation of subsurface changes in microstructure to resulting fretting wear of steels. Results from this study yield important insight into contact material degradation, and guide understanding of local hardness changes and appropriate material damage models associated with the contact area.

Microstructure changes can influence the response of a material to plastic deformation and, hence, influence the oxidation rate. Changes in oxidation rate may, in turn, alter the wear behavior. The role of oxidation during fretting wear and damage accumulation remains a controversial topic.\[40, 41, 42, 43, 44\] Fretting wear has been thought to mainly be an oxidative process; however, it has been observed that fretting wear occurs in materials that do not oxidize.\[45, 46, 47, 48, 49\] The significant increase of the wear rate with slip amplitude observed in the fretting wear regime (Figure 1.8) does not appear to coincide with an oxidative wear process, which is typically seen as a mild wear process, because the oxide scale usually acts as a lubricious (low adhesion) solid film,\[50, 51, 52, 53, 54\] slowing down the wear process. Eyre et al.\[55\] found a change in oxide wear debris of 0.4% carbon steel for various sliding speeds. Quinn\[56, 57\] proposed a parabolic theory of oxidational wear, where the oxide layer reached a critical thickness (1–3 μm) before rupturing to produce oxide wear debris. While many oxidational wear models assume a parabolic law,\[58\] inconsistencies between parabolic oxidation theory and experimental evidence led to the development of linear oxidational laws.\[59, 60\] Oxides have been found to form at ambient temperatures much below than the temperatures expected from phase diagrams. This may be explained by considering that the contact pressure developing over the real area of contact (which is the sum of all asperity-asperity contact areas spontaneously forming during sliding at the contact interface) can be several orders of magnitude higher than that predicted based on the apparent area of contact.\[50\] Excessive frictional heating at these asperity contacts (“hot spots”) is responsible for the observed oxide growth under ambient temperatures. Large temperature variations at these hot spots are believed to be responsible for the formation of different oxides,\[61, 62, 63\] although this is hard to prove due to the difficulty to measure these short-lived temperature spikes. However, oxidational wear promoted by mechanical stress/strain effects is much less understood than thermally-induced oxidational wear. If the “hot spot” theory is not adequate, a mechanical deformation driven oxidation mechanism could be the answer.

As discussed in previous sections, most wear models use the bulk material hardness as the mechanical property governing the wear rate of the material.\[64, 65, 66, 67\] However, the bulk hardness usually differs significantly than the surface hardness, because the surface undergoes
significantly more plastic deformation than the bulk during sliding and, even more, during fretting wear. These may be a reason for the varying conclusions about the correlation of hardness with wear rate.\textsuperscript{[68, 69, 70]} A more promising approach may be to investigate the correlation of material toughness with wear rate, or use the material toughness in certain fretting regimes and the hardness in others.\textsuperscript{[16, 71]} For example, if cracking is found to be more dominant in the mixed fretting regime, an appropriate material property to examine wear in this regime would be toughness, whereas in other regimes, the material hardness may be the more pertinent material property affecting wear.\textsuperscript{[72]}

The aforementioned wear mechanisms make up the major types of wear seen in most traditional industrial applications. Erosive wear can be considered another form of wear, but will not be discussed in this dissertation, as it is a special case where there is a need for a carrier medium to carry hard particles impinging onto a surface and causing loss of material by a one or several of the previous wear processes combined together.

Understanding the dominant wear mechanism(s) involved in a tribosystem is an important step to fully decipher the wear process. Fretting wear, similar to other forms of wear, combines one or more of these wear mechanisms. Fretting wear is often observed to occur by a combination of oxidational wear (a form of mild wear) and/or contact fatigue wear, although several other wear mechanisms (i.e., adhesion and abrasion) may also be contributing to the overall wear rates, at least during a portion of the wear life. I will discuss these studies in the following sections, with specific attention to the alloy of interest in this dissertation.

1.4 PROPERTIES OF STEELS

In this study, A216 carbon steel [ASTM A216/A216M] and 410 stainless steel [ASTM A314-15] were used as sliding countersurface materials. These steels are used in the W501FD engine row-2 compressor diaphragm of the Siemens turbine engine,\textsuperscript{[73]} where significant fretting wear problems have been found to cause loosening of the diaphragm, impact with the stator and, eventually, shut down of the engine for repair.\textsuperscript{[9]} The mated materials, i.e., diaphragm and casing, are made of these two different ferrous alloys. Since fretting wear failures are currently not well understood, a thorough analysis of the materials leading to understanding of the failure mechanisms was the objective of this dissertation.

The properties of steels are linked to their chemical composition, processing path, and microstructure resulting from processing.\textsuperscript{[74]} For a particular chemical composition, the properties of iron/steel can be varied by changing the microstructure. These properties are called “structure-sensitive” properties, and include properties such as yield strength and hardness.\textsuperscript{[74]} Materials engineering involves microstructural processing to achieve desired properties. Such microstructural processing generally involves some form of mechanical deformation (such as hot or cold rolling) and/or thermal treatment. However, there are many times when an unexpected microstructure can develop, resulting in properties different than those originally sought. These undesirable properties can lead to catastrophic and unexpected failures.

To understand the properties of a particular type of steel, it is instructive to consider the types of microstructures that can form in steels and the driving force(s) responsible for their formation. It
is also necessary to know what properties are desired for a particular application. Often, the desirable properties to be improved are inversely related to one another, thus making it difficult to optimize all the properties desired. For example, when the material hardness increases, its toughness generally decreases. Therefore, obtaining the optimal properties for a particular application requires insight into the mechanisms influencing opposing trends in material behavior. Moreover, it is often necessary to consider the desirable properties for manufacturing the part, which can be quite different than the desired material properties in the actual application. These and other issues must be addressed when seeking correlations between microstructure and material properties.

The constituents of ferrous microstructures typically include ferrite, martensite, cementite, austenite, pearlite, and bainite.

Ferrite is a solid solution of iron containing carbon and may contain one or more additional alloying elements, such as silicon, chromium, manganese, and nickel,[75] with a body-centered cubic (bcc) structure. Depending on whether the solid solution contains interstitial or substitutional elements, the ferrite may have different characteristics. Interstitial elements and/or an increase in grain boundaries can generally provide an increase in hardness,[76] whereas substitutional elements may or may not have much of a solid-solution hardening effect.[77] Because of the small size of interstitial atoms like carbon, diffusion is rapid. Larger substitutional atoms cannot in general diffuse as quickly, and this influences the progress of heat treatments applied to ferrous alloys. Control of grain size is generally carried out through thermomechanical treatments, a combination of mechanical deformation and annealing, which can be affected by alloying to pin grain boundaries during heat treatment.[74]

Cementite is an iron carbide with stoichiometry Fe₃C and orthorhombic lattice.[78] It contains 6.67 wt.% carbon and 93.3 wt.% iron, with carbon in the largest interstices. Cementite is a hard and brittle material that can form in all ferrous alloys and one of the two phases found in microstructural constituents known as pearlite, bainite, and tempered martensite. Many material properties associated with these microstructures are dependent on the quantity and morphology of cementite particles.

Martensite is a supersaturated solid solution of carbon in iron formed by rapid quenching from high temperatures. The amount of carbon in martensite far exceeds that found in ferrite, resulting in a distorted body-centered tetragonal (bct) crystal structure, instead of the bcc structure of ferrite. The continuous cooling–temperature (CCT) diagram shows that martensite only forms at high cooling rates in plain carbon and low alloy steels (only some high alloyed steels can form martensite by air cooling). Martensite tends to be very hard and brittle, and so tempering of martensite is usually carried out to restore some ductility and increase toughness. During tempering, the carbon that is in supersaturated solid solution precipitates onto preferred crystallographic planes (typically \{111\}) of the martensite lattice. With sufficient alloying, the martensite start temperature can be forced below room temperature, meaning incomplete transformation and retained austenite present in the steel.[74] To some degree, the hardness of martensite depends on the carbon content. Retained austenite is found when the carbon content increases above 0.4 wt% and, because austenite is softer than martensite, the hardness decreases
at carbon concentrations above this level. The yield strength also increases with carbon content and changes with lath martensite packet size.

Like ferritic stainless steels, martensitic stainless steels (such as the 410 stainless steel, used in this study) are high chromium alloys (12–18 wt% Cr), though both ferritic and martensitic stainless steels have lower chromium content than austenitic stainless steels. Martensitic stainless steels have carbon content in the 0.12–1.2 wt% range. With carbon and other alloy additions, such as nickel, austenite can exist up to 25 wt% Cr in martensitic stainless steels. They become martensitic on air cooling, even in thick sections, making them ideal for creating large engineering components, such as the casings in the Siemens turbine application. Martensitic stainless steels are considered high-strength stainless steels because they can achieve yield strengths between 550 and 1725 MPa. Ferritic stainless steels have microstructures consisting of ferrite and carbides and are not considered high-strength steels, because their yield strength is between 170 and 450 MPa.

Austenite does not exist at room temperature in plain-carbon and low-alloy steels, other than as small amounts of retained austenite that did not transform during rapid cooling. However, in certain high-alloy steels, such as austenitic stainless steels, austenite is the predominant phase. Manganese and nickel are alloying elements that stabilize austenite at room temperature. Austenite is a face-centered cubic (fcc) structure, which has certain desirable qualities compared to the bcc structure of ferrite. fcc alloys may possess low temperature toughness, excellent weldability, and are non-magnetic. Because of the high alloy content, austenitic steels are usually corrosion resistant. However, these alloys could be quite expensive due to required high concentrations of costly alloying elements, may exhibit susceptibility to stress corrosion cracking (certain austenitic steels), have relatively low yield strength, and cannot be strengthened other than by cold working, interstitial solid-solution strengthening, or precipitation hardening. Cold working can greatly increase yield strength and tensile strength at the expense of ductility. Carbon is not effective in strengthening austenite because the interstitial site in austenite is a regular octahedron and the corresponding strain field is similar to that of a substitutional solute.

Pearlite and bainite are combinations of ferrite and cementite in a parallel plate or lath configuration, known as lamellae. The difference between these two types of microstructures is in the fineness of the ferrite + cementite morphology. Pearlite has a coarse or fine morphology, at high or low formation temperatures, respectively. Bainite has very fine and parallel needles of ferrite separated by elongated particles of cementite. Bainite also has “upper” and “lower” variants depending on the temperature at which they are formed.

In addition to grain size, the properties of fully pearlitic steels depend on the spacing between the ferrite and cementite lamellae (interlamellar spacing λ) and colony size. The steel composition does not have a major influence on the yield strength of fully pearlitic eutectoid steel though there is some solid solution strengthening of the ferrite in the lamellae of the lamellar structure. The thickness of the cementite lamellae also has an influence on the properties of pearlite. Fine cementite lamellae can be deformed where thicker lamellae tend to crack during deformation. The wear resistance of pearlite arises from the lamellar distribution of ferrite and cementite (a hard constituent embedded in a soft and ductile constituent). The hard cementite plates do not
abrade away as easily as the equiaxed cementite particles found in other steel microstructures (tempered martensite). In general, the wear resistance tends to increase as the interlamellar spacing decreases, making the pearlitic interlamellar spacing one of the most important microstructural parameters for controlling hardness and wear resistance.\[74\]

Most common steels, however, have a ferrite-pearlite microstructure. In these steels the carbon content and the grain size determine the microstructure and resulting properties. The ultimate tensile strength steadily increases with carbon content, due to the increasing fraction of pearlite (much higher strength than ferrite). Yield strength, however, is relatively unaffected by carbon content due to the fact that yielding is mainly controlled by the softer ferrite matrix. Strength and toughness can be related to microstructural features. It has been found that finer ferrite grain size improves strength and toughness, pearlite increases tensile strength, nitrogen increases yield strength, but both pearlite and nitrogen reduce toughness.\[74\] Control of grain size is most commonly used to engineer the material properties of ferrite-pearlite steels.

Similar with pearlite, bainite is a composite of ferrite and cementite, with the ferrite having an acicular or feathery morphology and the carbides may be discrete particles. Because of these morphological differences, bainite has much different properties than pearlite. In general, bainite has higher strength. There are two forms of bainite, depending on temperature at which austempering is conducted; upper bainite (400-550°C) and lower bainite (250-400°C).\[82\] Upper bainite forms at lath boundaries and lower bainite forms on particular crystallographic habit planes within the laths. These differences in morphology mean that they have different mechanical properties; lower bainite, has a finer acicular structure and carbides within the laths and higher toughness than upper bainite with its coarser structure.\[82\] There is a rapid increase in tensile strength with the decrease of the transformation temperature increase amounts of lower bainite formed). The main characteristic with bainitic steels is that an optimal strength/toughness combination can be obtained without expensive heat treatments.\[74\]

Carbon steels, such as A216 steel, and low-alloy steels tend to be far less expensive and more formable than stainless steels, such as 410 stainless steel, which tend to be far stronger and corrosion resistant. Carbon steels can be made with increasing carbon content to increase hardness and strength, and improve hardenability. However, the higher the carbon content the more brittle the steel will be due to its tendency to form martensite. Alloying with other metals can improve strength, toughness, and other properties. Carbon steels are divided into four groups based on the carbon content: low, medium, high, and very high carbon content. Low-carbon steel (often called “mild steel”) has less than 0.30% carbon and is the most commonly used grade of steel. Low-carbon steels can be easily machined and welded and are more ductile than high-carbon steels, therefore are easier to shape.

The iron-carbon phase diagram shown in Figure 1.9 indicates that steels contain less than 2 wt% carbon. A very important composition is ~0.8 wt.% carbon, known as the eutectoid composition.
A216 carbon steel has less than 0.3% carbon content, making it a low-carbon steel of hypoeutectoid composition. The only phases in equilibrium from room temperature to 723° (in this composition range) are α-iron and cementite, most often found distributed as lamellae in pearlite.

Stainless steels generally contain a minimum of 10.5% chromium. They have high strength and durability and also provide excellent corrosion resistance. Stainless steels are significantly tougher than plain carbon steels at low temperatures. There are three types of stainless steels: austenitic, ferritic, and martensitic. Ferritic stainless steels have between 12% and 27% chromium with small amounts of austenite forming alloys. Austenitic stainless steels depend on alloying elements to stabilize the austenite phase at low temperatures. Nickel is the most important stabilizer, and others include carbon, manganese, and nitrogen. Martensitic stainless steels have the least amount of chromium and offer high hardenability. The stainless steel analyzed in this study (410 stainless steel) belongs in the martensitic stainless steel category. Because the corrosion resistance of stainless steels is better than that of carbon steels, they can be used in higher temperature applications, and they are often tougher than carbon steels. However, they are more expensive (due to their alloying elements) and harder to shape than carbon steels.

The properties of iron and steels are linked to their chemical composition, processing path, and resulting microstructures. The mechanical properties, such as yield strength and hardness, are structure-sensitive properties and, as the name would suggest, depend on the microstructure. Processing is a means to develop and control the microstructure of steels.\[74\]
deformation (present, obviously, in wear situations) also affects the microstructure of all steels. Most importantly, the existence of an unexpected microstructure can bring about unwanted properties in engineering applications, such as the turbine components examined in this study, and should always be considered when analyzing anticipated or observed behaviors in service.

The principal objective of this investigation was to determine the cause of excessive damage due to fretting wear between A216 carbon steel and 410 stainless steel (the materials making up the components in the W501FD engine row-2 diaphragm), with particular focus on A216 carbon steel. The present study was initiated to examine the combination of surface and subsurface properties, in an attempt to elucidate the underlying wear mechanisms involved in the fretting wear process and to understand the pertinent material microstructure and material properties so that to model the wear process in future. A more thorough understanding of the role of microstructure combined with a thorough analysis of the wear surface will lead to a significantly better understanding of the wear mechanisms that participate in the catastrophic failure of materials during fretting wear. Understanding fretting wear mechanisms is essential to provide industry with the knowledge necessary to prevent fretting damage.

Chapter 2

Material and Methods

2.1 SPECIMENS

Disks of 2 cm diameter consisting of A216 carbon steel and pins of ~1 cm diameter made of 410 stainless steel were used as specimens. Table 2.1 gives the composition of the pin and disk specimens. While chromium is merely one of the trace elements in the A216 carbon steel disk, but is 11.5–13.5% in the 410 stainless steel pin, it is ideal for analyzing transfer of pin material to the disk by spatially-resolved energy dispersive spectrometry (EDS). These steels are currently used as the diaphragm and casing materials, respectively, in the row 2 diaphragm of the W501FD engines of Siemens, in which significant and catastrophic fretting wear damage has been discovered. Polishing was performed with 240-1200 grit papers and then with diamond pastes from 6μm to 1μm, on both the pin and disk specimens. Polishing showed no effect on the wear behavior, and so various surface roughnesses were not analyzed in this dissertation.
Table 2.1. Composition of disk and pin specimens.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (at%)</th>
<th>A216 carbon steel disk(^1)</th>
<th>410 stainless steel pin(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.25–0.30</td>
<td>&lt;0.15</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>0.50</td>
<td>11.50–13.50</td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>0.7–1.2</td>
<td>&lt;1.00</td>
<td></td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.035</td>
<td>&lt;0.040</td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.035</td>
<td>&lt;0.030</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>0.60</td>
<td>&lt;1.00</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)ASTM A216/A216M
\(^2\)www.aksteel.com

2.2 FRETTING WEAR APPARATUS

Figure 2.1 shows the pin-on-disk testing apparatus (UMT3, CETR) used in the present study. The normal load, frequency of oscillation, and stroke length are the input parameters, whereas the friction force and lateral displacement are the measured parameters. Acoustic emission may be a valuable addition to future studies.
Normal loads of 2, 10, and 15 N were applied at a frequency of 5 Hz and stroke length of 120 µm for 1, 2, 12, and 69 h (steady state). Previous testing for smaller amplitudes of fretting wear revealed a linear variation in wear rate with amplitude. Fretting wear is typically encountered for stroke lengths of less than 200-300 µm; above this range the behavior changes from fretting to reciprocating sliding. Thus, the stroke amplitude was set at 120 µm to simulate fretting wear conditions characterized by both stick and slip behaviors for the load range used in this study. Because the force versus reciprocating distance hysteresis remained stable after testing for as long as 69 h, it is referred to as steady-state, while the transient responses obtained for testing times much less than 69 h are attributed to the so-called run-in stage of fretting wear. From the analysis of the energy hysteresis curves, the responses for 2 and 10 N loads were found to be in slip mode, whereas those for a load of 15 N were found to be in stick-slip mode.

2.3 PROFILOMETRY

The depth of each wear track was measured from two-dimensional surface profiles obtained with a KLA – Tencor™ (P-10 model) stylus profiler. The stylus has a conical diamond tip with a radius of 2µm. A low load (50µN) was applied to preserve surface integrity. The wear volume was calculated from three-dimensional profiles obtained with this same profilometer.

2.4 MICROANALYSIS METHODS

2.4.1 Analysis of worn surfaces

Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were performed with a Zeiss EVO-MA-10 scanning electron microscope with a tungsten filament operated at a voltage of 20 kV. The SEM was used to characterize the dominant wear mechanisms on the wear tracks. The x-ray analysis was conducted with an EDAX™ Genesis system having a silicon drift detector. This method was used to study surface oxidation due to fretting and material transfer.
from the pin to the disk specimen surface through mapping of chromium, which is much higher in the pin material.

2.4.2 Analysis of damaged subsurface

i. Focused Ion Beam (FIB)

For subsurface damage analysis, cross-sectional samples were obtained with a focused ion beam (FIB) and transmission electron microscope (TEM) FEI Quanta 3D SEM/FIB system using a gun voltage of 30 kV. Cross-sectional samples were obtained parallel and perpendicular to the wear track direction as schematically shown in Figure 2.2.

Figure 2.2. Sample configurations in relation to the direction of wear marks (slip direction).

Figure 2.3 illustrates the FIB milling process used to create the TEM cross-sectional samples. First, a protective platinum layer was deposited using Ga ion beam with a current density of 2pA \( \mu \text{m}^2 \) onto the sample surface and a rough trench was milled, using a current of 30 nA (as seen in Figure 2.3a). The current was gradually decreased to 0.5 nA as the beam distance from the sample surface decreased to minimize damage of the sample before extraction. When the thickness decreased to ~500 nm, the sample was removed and a u-trench was cut below the tilted sample (Figure 2.3b). A micromanipulator was then welded to the platinum layer and the remaining sample was milled free (Figure 2.3c). Subsequently, the sample was carefully maneuvered out of the trench with the micromanipulator and welded, using a platinum layer, to a copper TEM grid (Figure 2.3d). Finally, the micromanipulator was cut free from the sample (not shown), leaving the sample free to be analyzed by the electron microscope.
ii. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was used to examine the subsurface microstructure and wear features. TEM imaging was performed with a JEOL 2011 LaB₆ TEM operated at a voltage of 200 kV. The TEM was also used to study the oxide scale thickness, amount of subsurface porosity, damage depth, and dislocation substructure and distribution in the sample, including pertinent crystallographic orientations of substructural constituents with respect to bulk crystal structure using selected area diffraction (SAD).
Chapter 3

Results

Experimental results of this investigation are subdivided into two sections: (a) results from the analysis of surface wear features, and (b) results from the analysis of subsurface wear features. Since a typical analysis of wear surfaces requires a thorough surface analysis, this was conducted first. Much less (if any) analysis is typically also conducted on subsurface wear features, even though this should be an imperative aspect of wear analysis, in order to thoroughly understand the progression of wear mechanisms. A key feature examined in this study is the microstructure evolution in the course of reciprocating sliding.

3.1 SURFACE WEAR FEATURES

3.1.1 Effect of Normal Load

Figure 3.1 shows the dependence of the severity of fretting wear on normal load for a testing duration of 12 h. The first row of Figure 3.1 shows SEM micrographs of the wear scar produced due to sliding under a normal load of 2, 10, and 15 N, while the second, third, and fourth rows show corresponding EDS maps of iron, oxygen, and chromium, respectively. The SEM images and EDS maps indicate an enhancement of oxidation and material transfer from the pin specimen (shown in the chromium maps) on the wear scar with increasing normal load. The oxygen maps indicate that while oxidation of the sliding steel surface for a normal load equal to 2 and 10 N (slip) appears to be similar, it is more pronounced for a normal load of 15 N (stick-slip), suggesting that a transition from slip to stick-slip conditions due to the increase of the normal load was conducive to oxidation of the material. Material transfer from the pin to the disk surface (tracked by EDS) increased with normal load regardless of the occurrence of either pure slip (2 or 10 N load) or stick-slip (15 N load) contact conditions.

High-magnification SEM and EDS provided evidence of a change in dominant wear mechanisms from adhesive and abrasive wear at relatively low (2 N) or intermediate (10N) normal loads to abrasive wear and material transfer from pin specimen (due to adhesive wear of the pin) in the slip region of the disk at a high normal load (15 N) after testing for 12 h (Figure 3.2). The oxygen and chromium EDS maps confirm that the increase of the normal load promotes surface oxidation and materials transfer, respectively.

3.1.2 Effect of Sliding Time

Figures 3.3 and 3.4 show the evolution of fretting wear and oxide formation for a 10 N normal load (pure slip) and 1 or 2 h of testing, respectively. Material from the pin specimen (chromium maps) initially transfers to the disk where it becomes oxidized along with iron. Sliding for 1 and 2 h corresponds to the run-in stage of fretting wear, involving a progressively increasing conformability of the wearing surfaces and loaclaized high pressure spikes, as evidenced by the wear fetaures on the sliding tracks.
Figures 3.5 and 3.6 show the progression of fretting wear and oxide formation for a 10 N load (pure slip) after 12 and 69 h of testing, respectively. The longer duration of sliding has resulted in more uniform oxidation with less significant chromium transfer from the pin to the disk. However, after testing for 12 h, there are still some areas of heavier chromium transfer. After 69 h of testing (steady state), the surface has a much more uniform appearance in both oxidation and chromium transfer (very little chromium transfer from the pin to the disk and an extremely even layer of oxide on the surface).
Figure 3.1. SEM images (first row) and EDS elemental maps (second, third, and fourth rows) of the entire wear scar produced on the surface of A216 steel disk for a normal of 2, 10, and 15 N, 120 µm stroke amplitude, 2 Hz oscillation frequency, and 12 h testing time.
Figure 3.2. High-magnification SEM images (first row) and corresponding EDS elemental maps (second, third, and fourth rows) revealing characteristic wear features on the surface of A216 steel disk for a normal of 2, 10, and 15 N, 120 µm stroke amplitude, 2 Hz oscillation frequency, and 12 h testing time.
Figure 3.3. Low- and high-magnification SEM images (first row) and corresponding EDS elemental maps (second, third, and fourth rows) revealing characteristic wear features on the surface of A216 steel disk for 10 N normal load, 120 µm stroke amplitude, 2 Hz oscillation frequency, and 1 h testing time.
Figure 3.4. Low- and high-magnification SEM images (first row) and corresponding EDS elemental maps (second, third, and fourth rows) revealing characteristic wear features on the surface of A216 steel disk for 10 N normal load, 120 µm stroke amplitude, 2 Hz oscillation frequency, and 2 h testing time.
Figure 3.5. Low- and high-magnification SEM images (first row) and corresponding EDS elemental maps (second, third, and fourth rows) revealing characteristic wear features on the surface of A216 steel disk for 10 N normal load, 120 µm stroke amplitude, 2 Hz oscillation frequency, and 12 h testing time.
Figure 3.6. Low- and high-magnification SEM images (first row) and corresponding EDS elemental maps (second, third, and fourth rows) revealing characteristic wear features on the surface of A216 steel disk for 10 N normal load, 120 µm stroke amplitude, 2 Hz oscillation frequency, and 69 h testing time.
3.2 SUBSURFACE WEAR FEATURES

The microstructure of an unworn sample is shown in Figure 3.8 and is labeled “0N”. The initial microstructure is that of pearlitic steel.

3.2.1 Features of Cross-Sections Parallel vs. Perpendicular to Wear Direction

As you can see, in Figure 3.7, we have a hypoeutectoid microstructure, containing proeutectoid ferrite and pearlite, as we would expect in A216 steel, with bands of dislocations running through the two phases.

Figure 3.7. Bright field TEM images of subsurface features with cross-sections parallel and perpendicular to the wear direction with wear parameters of 15N, 12 Hr, 120 um, and 2 Hz
We find that a dislocation band (cell wall) structure develops below the surface. The most significant microstructural change appears to occur in a direction parallel to the wear direction, at an angle of approximately 45 degrees from the surface, so the direction parallel to wear is emphasized from this result forward. We also find that the oxide that has developed on the surface provides an uneven surface coverage.

### 3.2.2 Features with Increasing Applied Load

Preparation of the background sample by FIB was difficult, as it milled much faster, at the same current, than the deformed samples. Additional dislocations would increase the hardness of the surface making it more difficult to mill and thus easier to control the milling process by decreasing the milling rate. There was slight FIB damage at the surface of the background sample that was seemingly unavoidable, but the microstructure was still viewable.

The background sample showed a shallow (1-1.5 um) dislocation cell wall structure at the surface, probably due to the cutting of the disk at the Siemens factory, though any uneven dislocation distribution may initiate dislocation wall formation in certain materials. The area directly below this was unaffected.

In the 2N load, the dislocation cell walls become denser than the unworn sample with the angle remaining at 45 degrees. The 15N load appears to increase the density of dislocations and also remains at an angle of 45 degrees. The thickness of the wall isn’t of much use for comparison, as the thickness depends on the cut of the subsurface.

The oxide scale appears to be quite porous and uneven in both the 2N and 15N samples. Shear bands also develop directly below the oxide with both the 2N and 15N load, which could enable an easier removal of oxide from the wear surface.

As you can see in Figure 3.8 the 15 N applied load appears to have denser dislocation cell walls and fewer dislocations in the areas between the walls.
Figure 3.8. Bright field TEM images of subsurface features parallel to the wear direction, induced by deformation at 12 Hr, 120 um, 2 Hz at loads of 2, 10, and 15N.
3.2.3 Features with Increasing Time with 2N Load

Figure 3.9. Bright field TEM images of subsurface features parallel to the wear direction, induced by deformation at 0, 12, and 69 Hr, sliding distance of 120 um, frequency of 2 Hz, and a load of 2N.
Figure 3.9 shows dislocation cell configurations at 0, 12, and 69 hours fretting with an applied load of 2N. At 12 hours, the dislocation walls become denser than the unworn sample with the angle remaining at 45 degrees. At 69 hours the density of dislocations increases and the cell walls become spaced closer together. The angle of the dislocation walls has now rotated to close to parallel to the surface. There appears to be an even dislocation density between the walls as well.

The oxide scale at 12 hours appears to be quite porous, and exhibits uneven surface coverage while the oxide scale at 69 hours appears to be denser and evenly coats the surface, indicating possible oxidational wear occurring in a controlled manner. Shear bands also develop directly below the oxide, at 12 hours.

At 69 hours, there appears to be an area near the surface that has not developed dislocation cell walls. This is, possibly, due to a grain orientation that is more resistant to deformation.

At 69 hours we notice that there is no apparent pearlite structure in the areas where dislocation cell walls have formed.

### 3.2.4 Subsurface Wear Features of PIN (Parallel to Wear Direction)

The counterbody (the pin) shows no development of dislocation cell walls after 12 hours, at 2 N.

![Figure 3.10. Pin Overview and surface microstructures when worn with conditions of 2N, 12 Hrs, 120 um, 2 Hz - Parallel to wear direction](image-url)
3.3 IMAGE COMPILATIONS EMPHASIZING TRENDS

As seen in Figure 3.11, a wall-like (“persistent slip band”) structure emerges with increasing time.

![Image 3.11. Bright field TEM images of persistent slip bands formed with an applied load of 2N, frequency of 2 hz, and sliding distance of 140um at a.) 0 hrs, b.) 12 hrs, and c.) 69 hrs.](image)

Dislocation cell walls appear to form at varying depths, depending on applied pressure, as you can see in Figure 3.12.

![Image 3.12. Bright field TEM images showing an increasing depth of persistent slip band formation formed at 2Hz, 120um, after 12 hours of fretting wear at pressures of a.) 0N, b.) 2N, and c.) 15N](image)

Figure 3.13 shows a rotation of dislocation cells with time. The oxide present on the surface appears to be uneven at 12 hours and becomes uniform in thickness by 69 hours.
As you can see in Figure 3.14, the oxide at 12 hours is unevenly distributed on the surface. By 69 hours (steady state) we have achieved uniformity, unseen during previous time frames.
As we increased fretting time there was also a change in oxide color, from red to black, that occurred over the surface of the wear scar.

As you can see from the oxide mappings in Figure 3.15, the oxide formation, with time, increases in uniformity.

![Figure 3.15. Overview of oxidation of wear scar surfaces (at 10N, 2Hz, and 120 µm sliding distance) at a.) 1 hr, b.) 2 hr, c.) 12 hr, and d.) 69 hrs.](image)

**CHAPTER 4**

**Discussion**

Fretting wear is quite often described as being an “oxidational wear” process \[84, 85, 86, 87, 88, 89\]. In fact, it was initially described as “fretting corrosion” \[90\]. Fretting wear exhibits an increase in wear rate not seen in typical sliding wear processes that has, unfortunately, not been explained comprehensively. Oxides generally act as solid lubricants; consequently oxidational wear is considered a type of “mild wear,” which does not fit the conventional definition of fretting wear \[91\]. It is apparent that, in order to understand the fretting wear process, a thorough understanding
of the oxidation process and associated subsurface structural evolution is necessary. The findings presented here appear to show a synergy betweenoxidational wear and fatigue wear, the latter of which builds below the surface during the oxidational wear process. It is my theory that in certain situations, oxidational wear is the dominant wear mechanism because insufficient strain has been generated in the subsurface to promote massive failure. However, the subsurface dislocation structure may also have an effect on the formation of surface oxides. It is my theory that this dislocation structure generates different primary oxides with increasing time, and wear of the oxide layer is predominant. Sakrani and Sullivan [92] show that Fe3O4 minimizes wear and friction in dry wear of alloy steel. In other instances, the material may fail by separation of subsurface material, due to accumulation of subsurface dislocation cells.

4.1 DISLOCATION CELLS/PERSISTENT SLIP BANDS (PSBs)

There is substantial development of distinctive microstructure/subsurface features during the fretting wear process observed in this study. As seen in Figure 3.11, a wall-like ("persistent slip band") structure emerges with increasing time. Such a structure results from a spatial variation in dislocation density during subsurface deformation accompanying wear. A variation in dislocation density can bring about the formation of a polyganized dislocation structure through a process driven by reduction of total energy of the system [93]. These dislocation structures are common to heavily deformed metallic alloys, and have been found to occur during reciprocal sliding/rubbing of two surfaces in contact [94, 95]. When dislocations arrange themselves into a crystallographic planar "wall" configuration, they are most often found to persist in this morphology during subsequent plastic deformation. Dislocation walls of this type are therefore also known as "persistent slip bands." Alternatively, dislocations may arrange themselves into arrays that do not align so sharply, but form meandering interfaces known as dislocation cells or "subgrain boundaries" [93]. The driving force for the formation of both persistent slip bands and dislocation cells is the same, namely a reduction in total elastic energy of the system [93, 96].

It has been reported that a large proportion of the dislocation density is used to maintain geometric compatibility at the subgrain boundaries. These dislocations are therefore unavailable for hardening, explaining the observed decrease in strain hardening rate with increasing polyganization [97]. The material inside the cell walls tends to soften as the dislocation walls form, creating a strain at the dislocation wall/cell interface. This heterogeneous distribution of dislocation density develops under conditions of multiple slip (or primary slip plus strong secondary-slip activity) [98]. The cell walls are also sometimes referred to as subcell boundaries. The depth at which these subcell boundaries form appears to increase with increasing load as well, increasing the affected volume with increasing load. This type of distribution of dislocations could cause many issues when parts are in service. If a high enough stress/strain is reached, massive subsurface failure may occur at dislocation cell wall boundaries. The increased temperatures seen in service could increase the dislocation mobility, creating dislocation cell structures at an accelerated rate.

In order to understand dislocation cell formation we must understand the variables that affect cell formation.

For cell formation, dislocations must have sufficient mobility out of their slip plane, meaning the cell formation depends on several external and internal factors [99]. External factors include
stress and temperature. Internal factors include polycrystalline engineering elastic constants, Young’s modulus, shear modulus, bulk modulus, Poisson’s ratio, single crystal elastic coefficients, elastic stiffness, elastic compliances, stacking fault energy, and any other factors that determine a dislocation’s mobility out of its slip plane by cross slip and/or climb [100]. Climb is generally temperature assisted due to the fact that it is diffusion driven, but, similarly, could be driven by strain gradients. At room temperature, cross-slip is possible in both FCC and BCC metals. Cross-slip is also possible in HCP metals that have been alloyed or HCP metals have been heated to elevated temperatures. In Al the initiation of multiple slip and cross slip is easy and a 3-D cellular dislocation structure tends to form [100]. With BCC materials having up to 48 slip systems that are nearly close packed, there are a multitude of slip systems available for cross-slip to occur, enabling the formation of dislocation cell walls (persistent slip bands), much more readily than for FCC materials (which have 12 slip systems). Due to the multitude of readily available slip systems in BCC materials, they have been found to more readily form linear dislocation structures, where FCC materials (with fewer available slip systems) tend to form cellular (3-D) dislocation structures.

The formation of persistent slip bands (PSB’s) as a bulk phenomenon appears to occur as a general feature in many FCC metal single crystals, such as copper, nickel, and silver, as well as some BCC materials, such as alpha-iron and niobium [101]. The formation of this matrix structure, the nucleation of PSB’s, and the steady state deformation occurring in PSB’s are largely due to cross-slip, and long-range internal stresses [101]. However, pure BCC metals do not appear to show PSB formation, as a general feature. Under typical testing conditions, cyclic deformation of BCC metals occurs by the low-temperature deformation mode, characterized by low mobility of screw-dislocations and impeded dislocation multiplication [101]. However, a deformation mode similar to that in FCC metals, accompanied in some cases by the formation of PSB’s as a bulk feature, is found under special conditions: low strain-rate, elevated temperatures (below the regime of self-diffusion), and the presence of interstitial impurity atoms, as is present in A216 steel [101]. Kuhlmann-Wilsdorf [102] found a strain-rate dependence of persistent slip bands in BCC materials. In fretting wear, strain-rate depends on applied load, sliding distance, and frequency. Although slip bands may not be seen as a BULK feature in BCC materials, surface features can and do vary significantly from the bulk during wearing conditions.

The most important question regarding these substructural features is “how could failure, due to dislocation cell formation, occur?” To answer this question, we can decompose it into two parts: 1) How do these cells affect the oxidation of the material associated with failure at the surface; and 2) how might these cells lead to subsurface failure?

Dislocation cells could increase oxidation rate due to a sort of “channel” formation. Forests of dislocations are located in dislocation cell walls and dislocation cores allow for short circuit diffusion. An increase in oxidation rate, due to “channel” formation, could increase the quantity of certain oxides that form by oxygen limited migration. The oxide on the surface can either grow thicker or replenish quickly as the oxide is being removed during the wear process. Oxide growth is still limited by oxygen transport through the oxide layer when there is oxide coverage on the substrate, however, a dislocated structure will make metal cation migration harder, limiting metal ion diffusion and increasing short circuit oxygen diffusion at the dislocation cores.
thus enhancing formation of the oxides formed by anion diffusion (Fe$_3$O$_4$) and reducing formation of oxides formed by cation diffusion (Fe$_2$O$_3$).

The Pilling-Bedworth ratio ($R_{PB}$) (Equation 4) is a ratio that describes the volume change due to the formation of an oxide on the surface of a metal. It is often used to describe the stress generation in an oxide layer.

$$R_{PB} = \frac{V_{\text{oxide}}}{V_{\text{metal}}}$$  \hspace{1cm} \textit{Equation 4}

Where $V_{\text{oxide}}$ and $V_{\text{metal}}$ are the volumes of the oxide produced by oxidation for a given metal volume\textsuperscript{[103]}.

The degree of protection offered by an oxide is better if a.) the Pilling-Bedworth ratio is close to unity, b.) the thermal expansion mismatch between base metal and oxide is low, and c.) the diffusion rates of oxygen and metal ions through the oxide is low. The oxidation rates can be further retarded by adding alloying elements, which preferentially oxidize and form protective films\textsuperscript{[104]}. This means that oxidation may offer better protection in alloyed steel than plain carbon steel, such as A216 steel. Takeda et al.\textsuperscript{[105]} showed that the thermal expansion coefficient is lower for Fe$_2$O$_3$ than Fe$_3$O$_4$, however, at low temperatures they are very close in value.

For ferrous alloys, an increase in formation of Fe$_3$O$_4$ generates a weaker oxide than Fe$_2$O$_3$, on the surface, increasing the wear rate of the oxide layer. However, since the Pilling-Bedworth ratio is lower for Fe$_3$O$_4$, than it is for Fe$_2$O$_3$, the delamination of oxide from the substrate may be less than is seen in prior stages of fretting wear. Fe$_3$O$_4$ grows with the $[110]$ direction of the oxide parallel to the $[100]$ direction of the metal surface\textsuperscript{[106]} giving approximately 3\% lattice misfit while $\alpha$-Fe$_2$O$_3$ also has approximately 3\% misfit\textsuperscript{[107]}. Thermal expansion coefficients increase with increasing temperature, with magnitudes in the following ascending order: FeO, Fe$_3$O$_4$, and Fe$_2$O$_3$\textsuperscript{[105]}. This also suggests that Fe$_2$O$_3$ will delaminate before Fe$_3$O$_4$ or FeO, at the same temperature as the temperature is increased. Another possible theory is that as the microstructure is changing from a pearlitic steel structure to the dislocation cell structure as time progresses lowering the misfit strain between the oxide and substrate. A decrease in misfit strain in congruence with Fe$_3$O$_4$ preferentially forming, through decreased mobility of the metal cations and increasing the anion diffusion by short-circuit diffusion at the dislocation cores would explain the change in adherence of the substrate as well as evolution of oxide from Fe$_2$O$_3$ to Fe$_3$O$_4$ with time. As long as the rate of production of oxide is larger than the wear rate, wear in the oxide tends to dominate the overall wear rate. There is also some possibility of forming oxides preferentially, in the dislocation heavy areas of the dislocation cells, causing the material to become brittle in these areas. Oxide precipitate at the cell walls may occur due to enhanced diffusion down the dislocation cores, resulting in a supersaturation of oxygen.

Although polyganization reduces overall matrix strain, dislocation cells still suffer strain, which is localized in the cell walls. These strained areas are most likely to nucleate cracks, generating wear debris. A macroscopic strain field accompanies individual dislocations, and as they glide towards the cell walls a pressure builds up across the wall. When the dislocation cell walls are pinned, the walls act to generate non-uniform stress field\textsuperscript{[108]}, which determines where nucleation of new dislocations might occur. There is a higher flow stress associated with
“pinned” cell wall. The strain is roughly the same as for the case with free dislocation walls, but the flow stress required is considerably higher \cite{108}.

Essmann & Mughrabi \cite{109} found that during tensile and cyclic deformation, annihilation of both screw and edge dislocations occurred, which set natural limits to dislocation densities achieved by plastic deformation. They found, however, that these low limits did not seem to apply in the cases of persistent slip bands in cyclically deformed FCC single crystals, where a high dislocation density (about 2 orders of magnitude higher) was predicted to form \cite{109}. Dislocation cells appear to create a uniform dislocation density distribution over time. This distribution consists of highly dislocated walls enclosing areas that are relatively “dislocation free”. This dislocation density may, eventually, saturate if failure in the subsurface does not occur before saturation.

Figure 4.1 graphically shows the 3 stages of work hardening in a single crystal as a function of resolved shear stress, \(\tau_R\), and shear strain, \(\gamma\). In a single crystal, slip occurs in 3 stages: stage I single slip; stage II work hardening; and stage III saturation. In stage I, slip occurs at low stress on a single, primary slip system. In stage II, slip induced by higher stress occurs on multiple slip systems that can interact in ways to inhibit further glide, resulting in hardening. In stage III, the applied stress is high enough to overcome the obstacles to dislocation motion until the work hardening saturates.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.1.png}
\caption{Figure 4.1 Stages of work hardening in a single crystal as a function of resolved shear stress, \(\tau_R\), versus shear strain, \(\gamma\) \cite{110}.
}
\end{figure}

In polycrystalline deformation the situation is more complex. Random crystallographic orientations of grains disrupt the direction of slip from one grain to the next. Slip can only occur across grain boundaries when properly oriented slip planes are contiguous. Stage I slip is therefore not seen in polycrystalline materials. Furthermore, an additional stage (stage IV) must be added to the plot in polycrystalline materials, to account for the observed, almost constant, low work-hardening rate and the capacity to accommodate large strains observed in polycrystalline materials \cite{102}. Stages II, III, and IV vary in their work hardening rates; in stage II the work hardening rate is constant but has a high value, in stage III the work hardening rate decreases sharply with strain, and in stage IV large plastic strains occur at a very low, virtually
constant work hardening rate. Initial formation of dislocation cell walls can occur in stage II. At low to medium strains (stage III work hardening) the cell walls are formed at approximately 45 degrees from the wear direction, aligning with the shear stress, confining softer dislocation free regions between these walls. When analyzing persistent slip bands, Brown \cite{111} reports that cross-slip occurs at all stages in the stress–strain curve, but at the onset of stage III, every screw dislocation cross-slips to annihilation, eliminating all screw dislocation dipoles. On this model, the absence of screw dislocations in the microstructure signals the onset of stage III. Stage IV is characterized by a nearly constant hardening rate, which depends only slightly on temperature and strain rate, and the hardening rate scales with the “would-be” saturation shear stress and ranges from 0.05-0.10 \cite{112}. It would make sense that in stage IV, (high strain situations), the dislocation cell walls rotate parallel to the rolling direction, due to the softer nature of the “dislocation-free” cell interiors. As the cells are rotated, new slip systems would become activated, enabling an even denser dislocation density to form. Estrin, Y., \textit{et al} \cite{112} found that a plateau of the hardening rate versus stress diagram associated with stage IV is followed by a fall-off, signifying yet another stage of hardening, referred to as stage V, which eventually leads to stress saturation. They found, in their model, that the dislocation densities in the cell interiors couldn’t be neglected with respect to the cell walls (the ratio of the two dislocation densities increasing from 10 to 35 with increasing strain). They also found that in stage IV hardening the cell interiors becomes more and more “dislocation free” (when compared to the walls) while forcing the dislocations into a smaller and smaller volume of the walls \cite{112}.

Dislocation cell walls appear to form at varying depths, depending on applied pressure, as you can see in Figure 3.12. With increasing pressure an increasing depth of dislocation cell walls are formed, due to the depth at which dislocations can now be produced and moved. Depending on the slip regime (and number of cycles reached), this may or may not cause catastrophic subsurface failure in a larger volume of material. There doesn’t appear to be a difference in angle of dislocation cell wall formation or a significant increase in dislocation density at dislocation cell walls with increased pressure, although a denser packing of dislocations at cell walls appears to be present.

Figure 3.13 shows a rotation of dislocation cells with time. Dislocation cells rotate with time/continued wear. This rotation could affect wear in many ways, among them being: 1) changes in oxidation rate, 2) changes in subsurface failure/crack propagation, and 3) activation of additional slip systems.

Rotation of dislocation cells could affect the oxidation rate in several ways. If the dislocation cell walls are in fact areas that promote an increased oxidation rate, a dislocation cell wall that is perpendicular to the surface would cause a localized increase in oxidational rate at various points in the oxide surface, causing some areas to oxidize faster than others. As these dislocation rich walls are rotated parallel to the surface, paths for enhanced oxygen diffusion are no longer oriented perpendicular to the surface, resulting in to a more uniform oxide thickness.

A crack propagates along the direction of travel of the asperity/contact above the crack. During sliding, the area in front of the contact is subject to compressive stresses, pushing that portion of the crack shut, while the area directly in back of the asperity/contact is subject to tensile stresses, opening the crack farther. Crack propagation, theoretically, would be greatest at 45 degrees,
when the areas of high strain align with the direction of maximum shear stress. McClintock, while investigating crack behavior in a rail under rolling conditions, has concluded that cracks in compressive fields tend to grow in shear. Forsyth found that initial cracks formed when the slip planes of PSBs most closely aligned with the maximum shear stress direction. However, as wear progresses, and dislocation cell walls increase in size and magnitude of accumulated strain, a lower applied stress can initiate crack propagation along dislocation cell wall interfaces. If the dislocation cell walls are rotated parallel to the wear surface, fatigue cracks could still propagate. Experimental results of Jahanmir et al. found that, in delamination wear, cracks propagated parallel to the surface for considerable distances before they became loose. Fatigue cracks could be affected by the rotation of the highly strained cell boundaries parallel to the wear direction, especially if cracks are initiated in the shear direction and then continue to propagate with the tensile forces seen by the crack at the trailing end of sliding during fretting wear. Fatigue cracks could then propagate at a more rapid rate with increased cycling.

Rotation of dislocation cells, in theory, will make activation of various slip systems easier because, now, many more slip systems will align with the maximum shear stress as the cells are being rotated.

Progression of wear with the growth of dislocation cells/persistent slip bands can lead to a multitude of failures, depending on the growth characteristics of the cells and the stress distribution/wear conditions.

A plausible theory follows. Many low amplitude movements can cause wear in the stick-slip regime. Much of fretting wear, where fatigue damage is present, appears to occur in the stick-slip regime. As wear continues, and material loss becomes more significant, we may see a shift in stress distribution and slip regime. If a change in the stress distribution occurs due to change in material contact conditions, for example, the same type of massive failures seen in the partial slip or mixed slip regimes could be seen, due to the fact that the dislocation cell structures are still forming subsurface. A high stress could tear apart the, already highly strained, subsurface structure. These increased wear rates won’t be as large of a problem in reciprocating wear, a gross-slip regime with a subsurface stress distribution different from that in the stick-slip or slip regime. In the case of carbon steel, under gross slip conditions, little difference is observed in either wear rate or wear scar topography at both low and high frequency. In gross-slip the same stress distribution seen in partial-slip or stick regimes is not seen and the same microstructural developments and/or failure modes may not occur. Further work in this area of study is highly suggested.

If we are claiming that fretting wear is a balance between oxidational wear and subsurface failure at dislocation cell walls then, theoretically, a massive failure could also occur if the oxidational wear rate is slower than the rate of dislocation cell wall growth at which a maximum density of dislocations is achieved. Since dislocations continue to be produced during plastic deformation, the “dislocation free” areas may eventually be consumed by the dislocation dense cell walls and there is possibility of massive subsurface failure.
Another possibility is that as long as the dislocation cell walls remain at an angle of 45 degrees, crack propagation can dominate wear behavior. When the dislocation cell walls rotate to an angle parallel to the surface, and oxidation rates increase as well as new forms of oxide occurring, oxidational wear takes over. Subsurface failure (by crack propagation) can still occur if the appropriate stresses are reached at the cell wall boundaries.

### 4.2 MICROSTRUCTURE DEVELOPMENT

Figures 3.9 and 3.11 show an intriguing microstructural development with increasing time. A216 steel is a hypoeutectoid steel, meaning it is comprised of proeutectoid ferrite and pearlite at ambient temperatures under equilibrium conditions. The microstructures observed at times 1 hour -12 hours are consistent with this microstructure. As we reach steady state wear, at 69 hours, we can see a marked absence of the pearlite phase, with a uniform phase in the cell interiors.

A possible theory for this transformation follows. Pearlite is a lath structure of eutectoid ferrite and cementite. The pearlitic microstructure has many phase boundaries, and therefore many dislocations may be associated with it. As the dislocation cell walls are formed, the dislocations from the cell interiors, including those associated with the pearlite microstructure, are driven towards the lower energy configuration of the cell wall, effectively dissolving the pearlite structure. The carbon from the cementite structure would be either redistributed into the cell interiors, supersaturating the ferrite with carbon, or follows the dislocations to the dislocation cell walls.

Dissolution of the pearlite structure could have many implications. If it is redistributed into the cell interiors the ferrite would show an increase in hardness. However, since ferrite has a low carbon solubility limit it would be more energetically favorable for the carbon to migrate with the dislocation cores to the dislocation cell walls, leaving behind a malleable ferrite cell interior. Since finer ferrite grain sizes improve strength and toughness in ferrite-pearlite microstructures, the dissolution of pearlite into the dislocation cell structure causes an effectively larger grain (the cell interior) to form, so the strength and toughness of the A216 steel decreases. Ferrite is the softest phase in steel, and so the cells could be easily distorted with further wear. This would explain the fact that the dislocation cell walls appear to have rotated to a direction parallel to the surface, with time.

Figure 3.10 shows the microstructure of the 410 stainless steel pin with 2N-applied load, after 12 hours of fretting. As you can see, the microstructure is only damaged in the top 500-700nm. No dislocation structure is present, indicating that the alloying of steel may have a significant effect on the fretting fatigue of the steel in question. Since alloying of steel creates a significant strain field the dislocation motion is impeded and the dislocation structure is less favorable.

### 4.3 WEAR OF OXIDE LAYER

The formation of a stable oxide layer can create a solid lubricant, changing the adhesion characteristics between contacting surfaces. A change in composition of the disk surface (changing the solubility between pin and disk) would cause a decrease in adhesion of pin to disk,
so we would expect adhesive wear to decrease and another wear mechanism, such as oxidational wear, abrasive wear, or fatigue wear, to dominate.

Figures 3.3-3.6 shows that at a 10N loading the wear mechanisms appear to vary from adhesive, abrasive, and fatigue wear of the oxide and substrate, at 1-12 hours, to mainly abrasive wear of the oxide layer and some transfer of pin material to disk (adhesive wear), at 69 hours. This abrasive wear of the oxide layer may remain dominant if the oxidation rate remains faster than the abrasive wear rate, and no other mechanisms develop with time.

Oxide formation is a complex process described by many theories: the early diffusion theories, such as Tammann-Pilling-Bedworth Parabolic Law (growth by uncharged particles) and Wagner Theory (diffusion of charged particles) \cite{123}, electronically driven theories, such as the theory of Cabrera and Mott \cite{123} and Schennach et al. \cite{124} and stress/strain limited theories \cite{125, 26, 126}. It is generally accepted that iron and many of its alloys oxidize in a layered structure with varying stoichiometries \cite{127, 128, 105}. Closest to the iron substrate is wustite (FeO), followed by magnetite (Fe$_3$O$_4$), then farthest away, hematite (Fe$_2$O$_3$). The growth of FeO and Fe$_3$O$_4$ is controlled by the outward diffusion of cations, whereas the growth of Fe$_2$O$_3$ at the Fe$_3$O$_4$/Fe$_2$O$_3$ interface is dominated by the inward diffusion of anions \cite{129, 130}. More recently, others have suggested that Fe$_2$O$_3$ grows by outward cation migration \cite{131, 132}. Wustite is only thermodynamically stable above 570°C. At temperatures below this, wustite decomposes into magnetite and alpha-iron. Cation and anion migration is accelerated at higher temperatures, however anything that can improve the diffusion rates of these ions enhances oxide growth. There is much controversy as to what temperatures are actually reached in the wear process. It is difficult to experimentally determine exact temperatures during the wear process, though some have attempted to assess this using infrared technology \cite{133, 134, 135, 136}. Many believe there are “hot spots” that form at the surface, due to the asperities that exist on the virgin surface and those that are created during the wear process. Others have shown that only modest temperatures are reached during the wear process. Since wustite is not found in our system, through x-ray diffraction of the wear particles, it is likely that temperatures of 570 degrees are not reached in any of our experiments.

During mechanical deformation in the plastic regime, dislocations are nucleated and propagated to accommodate strain. Many believe that oxidation is a stress/strain-aided or hindered process \cite{26, 125, 137, 126}. Stresses that build up in the oxide as it thickens can halt further oxidative growth \cite{125, 26}. Dislocation density, oxide thickness, and lattice misfit between oxide and substrate affect stress-driven oxidation. Grain boundaries/dislocation cell walls are areas where diffusion is promoted and higher strain energy may be seen, increasing possible strain-driven diffusion processes.

As you can see from the oxide mappings in Figure 3.15, the oxide formation, with time, increases in uniformity. X-ray diffraction of the wear particles indicates a mix of Fe$_3$O$_4$ and Fe$_2$O$_3$ particles, though a small percentage of FeO may have been undetectable by our instrument. This change to a uniform oxidation may indicate some change in primary oxide formed, changing the Pilling-Bedworth ratio and thermal coefficient of expansion which would change the oxide-substrate adhesion, with increasing time, leading to a less stressed oxide-substrate interface, and the ability to retain a cohesive oxide layer on the surface. Viewing the sample cross-sectional orientations using transmission electron microscopy we can also see this
difference in oxide thickness. As you can see, in Figure 3.14, the oxide at 12 hours is unevenly distributed on the surface. By 69 hours (steady state) we have achieved uniformity, unseen during previous time frames. As the dislocation cell structure becomes more pronounced and the dislocations pile up to form cell walls the dislocation cores can serve as pathways for oxygen transport, into the substrate, promoting the formation of Fe$_3$O$_4$.

The oxide debris changed from a reddish color to a blackish color with increasing time. This intimates a change in oxide formation at the surface as wear progresses. Hematite (Fe$_2$O$_3$) is a reddish oxide and magnetite (Fe$_3$O$_4$) is a black oxide.

All features seem to indicate a change in oxide formation with increasing time. When we analyze the oxide formation in terms of ion migration, we can come to a sufficient explanation as to why this happens. Any form of disruption to the matrix in which these ions are traveling, such as introduction of dislocations or formation of dislocation clusters, can change the rate of oxide formation. Creation of dislocations, during the wear process, could trap iron cations, preventing them from traveling outwards towards the surface, decreasing the volume fraction of FeO or Fe$_3$O$_4$ forming at the surface. However, with the creation of channels, such as those made available by dislocation cell walls, an increase in oxygen anion transport is possible, increasing the amount of Fe$_3$O$_4$ formed at the surface of the iron sample. The rotation of these cell walls with increasing time would have an influence on the diffusion of oxygen into the subsurface, enabling an increased oxidation rate parallel to the oxide surface, versus perpendicular to it. Thus, with increasing wear time and/or pressure we may see a shift in major oxide formed at the surface of our wear specimen. A shift in major oxide formed at surface affects the wear properties of that surface. In our fretting wear experiments we found that with time a much more even surface coverage developed, that did not appear to be completely removed from the subsurface at any point on the wear surface.

According to Schutze$^{[138]}$ the elastic moduli of Fe$_3$O$_4$ and Fe$_2$O$_3$ are similar (208 and 219 GPa, respectively), but fracture toughness varies more significantly. The fracture toughness of Fe$_3$O$_4$ is 1.4 MPa and Fe$_2$O$_3$ 1.6 MPa. Chicot et al.$^{[139]}$ verified elastic constants by experiment and molecular dynamic simulations, revealing a significant difference in elastic constants between Fe$_3$O$_4$ and Fe$_2$O$_3$. Comparison of hardness values by Takeda et al.$^{[105]}$ show that Fe$_3$O$_4$ and Fe$_2$O$_3$ have significantly different values of hardness, whether formed on an iron substrate or created by a sintering process, at all temperatures studied. Fe$_2$O$_3$ is a much harder species of iron oxide than Fe$_3$O$_4$, which is therefore expected to result in much different wear properties.

Regardless of the formation temperature, and whether or not the oxide is formed by sintering or standard oxide growth, the hardness of Fe$_3$O$_4$ is less than that of Fe$_2$O$_3$. Since the oxide appears to vary from the hematite (Fe$_2$O$_3$) form to the magnetite (Fe$_3$O$_4$) form with time during fretting wear, the corresponding decrease in hardness will have a significant effect on protection of the wearing surface. Sakrani and Sullivan$^{[140]}$ based their study on the idea that mechanically stable films of Fe$_3$O$_4$ formed by a balanced diffusion of both anions and cations into the film that make the bulk of the oxide more stable, and the adhesion with the metal substrate strengthened. In contrast, however, they found that the Fe$_2$O$_3$ films are less stable because the Pilling-Bedworth ratio is high (~2.14) signifying that the large apparent internal stress, coupled with the expansion of the lattice due to oxide growth by anion migration, leads to the loss of metal/oxide adhesion,
resulting in a thinner oxide overlayer. This would explain why the oxide remains uniform over the entire surface during the later stages of fretting wear, but is uneven and discontinuously removed in the earlier stages of fretting wear. This uneven removal of oxide could also be explained by an uneven pressure distribution at earlier stages of fretting wear, however the shift in color of the wear debris with time seems to imply the former. A shift to a softer oxide could also lead to a faster oxidational wear rate and lower spallation, due to the decrease in the Pilling-Bedworth ratio. As long as the rate of oxide formation surpasses the rate of oxide removal, an even oxide coating can be anticipated.

It is important to note, however, that while the wear mechanisms on the surface show various wear mechanisms such as abrasive wear of the oxide layer as the dominant wear mechanism, Figures 3.8 and 3.9 show that the subsurface has a possibly problematic structure developing with both increasing time and increasing load. The dislocation cells forming subsurface may be subject to a massive failure if the cell walls reach appropriate strain levels for crack formation. This means that it is possible that fatigue of the subsurface could become the prominent failure mechanism, under appropriate conditions, while it appears that abrasive wear of the oxide is the dominant mechanism. Testing longer than 69 hours is necessary to test this hypothesis.

4.4 TRANSFER OF 410 STAINLESS STEEL PIN TO A216 CARBON STEEL DISK

The transfer of the 410 stainless steel disk to the A216 carbon steel disk can be seen in Figures 3.1-3.6. Since 410 stainless steel has much higher chromium content than A216 carbon steel, the chromium serves as an excellent marker to determine transfer of pin material to the disk, during fretting wear. Note should be made that there is some chromium in the A216 steel, and so there will be a background level of chromium seen outside the wear scar in all cases.

Figures 3.1 and 3.2 show the wear progress at 12 hours for loads of 2N and 10N, in the slip regime, and 15N, in the stick-slip regime. We observe increasing transfer of chromium with increasing load in the slip-regime; at 2N load there is little to no transfer of pin material to disk. As we move from the slip-regime to the stick-slip regime we find an even heavier transfer of chromium to the center of the wear scar. This follows from the fact that shear stress seen by the pin is much higher in the stick-slip regime, thereby removing more of the pin material and transferring to the disk.

Figures 3.3-3.5 show the wear progress from 1-12 hours at 10N in the slip regime. We see a heavy transfer but uneven distribution of chromium on the A216 carbon steel disk. Figure 3.6 shows the surface when steady state wear, at 69 hours, has been reached; we find that the chromium is evenly distributed, but transference is lesser than in the wearing-in cases. This follows from the fact that the pressure is unevenly distributed during the wearing in cases, because the surfaces do not mate perfectly. Undulations present on the initial sample surface as well as from uneven wear, due to adhesion/fatigue/abrasion, create areas of higher pressure, and hence higher material transfer.
Chapter 5

Conclusions

The findings presented in this dissertation show that fretting wear is best understood as a synergy between oxidational wear and fatigue wear, the latter accumulating in effect below the surface during the oxidational wear process. In low load regimes, oxidational wear is the dominant wear mechanism when there is not enough subsurface strain to cause massive failure. Nevertheless, the dislocation structure forming in the subsurface has an effect on surface oxide formation. This causes a change in oxide stoichiometry over time. In high load regimes, the material may fail by delamination within the subsurface, due to accumulation and alignment of dislocation cell walls.

Though the exact pressure reached with applied load is hard to determine, we can characterize our findings by behavioral regimes. The "slip" regime is associated with pressures in the 2N to 10N range, while the "stick-slip" regime is associated with pressures in the 15N range. The depth of subcell boundaries increases with increasing load, indicating that in both the slip regime and stick-slip regime, dislocation cells are generated. These dislocation cells consume a larger portion of the subsurface as we transition from slip to stick-slip regimes. The depth of damaged layers is dependent on the non-uniform shear stress distribution, which varies with depth into the subsurface.

The dislocation cells also increase in depth over time within the slip regime. This indicates that the wear rate is slower than the formation rate of dislocation cells, suggesting that in longer time regimes, catastrophic failure could result from cell wall induced subsurface delamination. With time, the dislocation cells rotate from alignment with the maximum shear stress to a direction parallel to the surface. This rotation can affect crack formation/propagation as well as oxide formation on the surface, with implications for service lifetimes in engineering components subjected to fretting wear.

At 2N loading, in the slip regime, energy dispersive spectroscopy reveals that oxide formation during fretting wear is non-uniform in the early stages and becomes uniform by the steady-state wear phase, at 69 hours. The TEM cross-sectional images confirm this. It is concluded that the primary oxide evolves from Fe$_2$O$_3$ to Fe$_3$O$_4$, with increasing fretting time, leading to a uniform oxide on the surface of the A216 disk. This change in oxidation is believed to be associated with the formation of dislocation cells in the subsurface. The dislocation-rich cell walls serve as enhanced diffusion sites for transport of oxygen ions into the metal, increasing the percent of Fe$_3$O$_4$ formed on the surface. Though the hardness of Fe$_3$O$_4$ is less than Fe$_2$O$_3$, the Pilling-Bedworth ratio is smaller, thus leading to less stress generation in the oxide layer, and better adhesion to the A216 steel substrate. As long as the rate of oxide formation surpasses the rate of oxide removal, an even oxide coating can be anticipated.

Scanning electron microscopy combined with electron dispersive spectroscopy reveals that the wear mechanisms at 2N loading appear to vary from adhesive, abrasive, and fatigue wear of the oxide and substrate at 1-12 hours, to mainly abrasive wear of the oxide layer at 69 hours. While
the wear mechanisms on the surface confirm these forms of wear, the subsurface shows a possible problematic structure developing. The dislocation cells forming subsurface may be subject to a massive failure if the cell walls reach appropriate strain levels for crack formation. This observation shows the importance of surface combined with subsurface analysis for future endeavors to understand the wear process.

Chapter 6

Recommendations for Further Work

Our focus, in this dissertation, was on the short-term structural changes induced by the fretting process. It did not simulate the exact environment in which the W501FD row-2 diaphragm operates.

The research that has been undertaken for this dissertation has highlighted a number of topics on which further research would be beneficial. These include whether or not the dislocation structure becomes problematic at fretting times longer than 69 hours, at ambient temperature. With increased wear, does the dislocation structure begin to fail at the dislocation cell walls or through the cell interiors or does abrasive wear of the oxide remain the dominant wear mechanism? Further study of the oxide development on the surface of the wear scars, at the temperatures observed in service in the area of the row-2 diaphragm, would be beneficial. An increase in temperature will not only increase oxidation rates, but also increase dislocation mobility. Future studies might, for example, look for variation in dislocation cell structure with increased temperature. Does this structure maintain the dislocation wall structure at higher temperatures? If the dislocation wall structure forms at a faster rate during high temperature fretting does the dislocation wall continue to increase in thickness or does the structure reach a stage where the wall thickness becomes constant and continued wear causes failure at the dislocation cell walls? Further investigation into the evolution of oxide formation on the wear surface with an increase of temperature is recommended. An increase in temperature will increase the oxidation rates of the various oxides formed. Does this increase in oxidation rate create a protective layer faster than it is removed, at higher temperatures? As the dislocation cells evolve does abrasive wear of the oxide remain the dominant wear mechanism? If the temperature is increased, and FeO becomes an energetically stable form of oxide on the surface, does the oxide adhere to the substrate better, or does thermal expansion aid in removal of the oxide? Further fretting testing of the pin material (410 stainless steel) is recommended in order to determine the effect of alloying on the dislocation structure formed, since the pin material does not show any dislocation structure after 12 hours of fretting.
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