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An investigation of basic mechanisms of sliding friction and wear of implanted metals

Zhang, Lihua, Ph.D.
The Ohio State University, 1993
AN INVESTIGATION OF BASIC MECHANISMS OF SLIDING FRICITION
AND WEAR OF IMPLANTED METALS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

By
Lihua Zhang, B. S., M. S.

* * * * *
The Ohio State University
1993

Dissertation Committee:
D. A. Rigney
G. Meyrick
S. Smialowska

Approved by

D. A. Rigney
Advisor
Materials Science & Engineering
To My husband YaLin Wei
and my parents YaSong Zhang & XiuLan Li
and the rest of the family
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VITA

March 17, 1964 ------------------------ Born, Jilin, P. R. China

September, 1984 ---------------------- B. S., Metal Materials and Heat-Treatments, Jilin University of Technology, Changchun, China

September, 1986 ---------------------- M. S., Information Engineering, Jilin University of Technology, Changchun, China

1986 -- 1988 ------------------------- Teaching Faculty, Information Engineering Department/Metal Materials Department, Jilin University of Technology, China

January, 1991 ------------------------ M. S., Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio

1991 -- Present ---------------------- Graduate Research Associate, Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio
FIELDS OF STUDY

Major Field: Materials Science and Engineering

Studies in Tribology
   Prof. D. A. Rigney

Studies in Physical Metallurgy
   Profs. P. G. Shewmon, G. Meyrick, S. A. Dregia, C. E. Mobley

Studies in Mechanical Metallurgy
   Profs. P. M. Anderson, R. H. Wagoner

Studies in Chemical Metallurgy

Studies in Corrosion
   Profs. S. Smialowska, B. E. Wilde

Studies in Electron Optics and Metal Physics
   Profs. W. A. T. Clark, D. A. Rigney, H. L. Fraser
TABLE OF CONTENTS

DEDICATION................................................................................ ii

ACKNOWLEDGMENTS........................................................................ iii

VITA .................................................................................... v

FIELDS OF STUDY........................................................................ vi

LIST OF FIGURES .......................................................................... x

LIST OF TABLES .............................................................................. xviii

CHAPTER .................................................................................. PAGE

I INTRODUCTION........................................................................ 1

1.1 Background.............................................................................. 1
1.2 Objective of This Study.......................................................... 2
1.3 Approach................................................................................ 3

II LITERATURE REVIEW............................................................. 5

2.1 General.................................................................................. 5
2.2 Friction Models....................................................................... 6
   2.2.1 Introduction.................................................................... 6
   2.2.2 Adhesion Theories of Friction........................................ 9
   2.2.3 Deformation Models of Friction....................................... 11
       2.2.3.1 Asperity Deformation Model......................... 11
E  A SUMMARY OF THE RESULTS OF 52100 (1/8")/Fe AND 52100/Fe(Cu)........................................... 200

F  APPROACHES IN SOLVING THE Si PROBLEM............. 204

G  THE RELATIONSHIP OF FRICTION FORCE MEASURED AND THE THICKNESS OF THE STRAIN GAUGE BACKING BEAM............................... 206

REFERENCES ................................................................. 209
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Variation of the friction with the applied load</td>
<td>7</td>
</tr>
<tr>
<td>2.2</td>
<td>Dependence of the friction on the surface roughness</td>
<td>8</td>
</tr>
<tr>
<td>2.3</td>
<td>Types of contact, (a) adhesion, (b) plowing, (c) asperity interlocking</td>
<td>10</td>
</tr>
<tr>
<td>2.4</td>
<td>Friction coefficient vs. k, in the adhesion theory</td>
<td>12</td>
</tr>
<tr>
<td>2.5</td>
<td>The friction coefficient vs. k by Edwards and Halling</td>
<td>14</td>
</tr>
<tr>
<td>2.6</td>
<td>Definition of $\alpha$ by Challen and Oxley</td>
<td>14</td>
</tr>
<tr>
<td>2.7</td>
<td>Friction coefficient vs. $a$ and $f$ by Challen and Oxley</td>
<td>15</td>
</tr>
<tr>
<td>2.8</td>
<td>$F(u)$ vs. $u$ in the energy-based model of (21)</td>
<td>16</td>
</tr>
<tr>
<td>2.9</td>
<td>Atomic Configuration generated by a molecular dynamics simulation</td>
<td>19</td>
</tr>
<tr>
<td>2.10</td>
<td>The contact between two elastic solids in the presence of surface forces</td>
<td>24</td>
</tr>
<tr>
<td>2.11</td>
<td>An illustration of the ion implantation process</td>
<td>30</td>
</tr>
</tbody>
</table>
2.12. The dependence of range $R_p$ and range spread $\Delta R_p$ on the incident ion energy $E$, electron number of the ion and the substrate $Z_1, Z_2$, atomic mass of the ion and the substrate $M_1$ and $M_2$.  

3.1. Vertical Pin/ball-on-disk setup  

3.2. Pin-on-Disk geometry  

3.3. Modified loading system for low load.  

3.4. Schematic illustration of the joint for loading arm. (A) original (B) modified.  

3.5. Disk and pin dimensions  

3.6. A schematic illustration of the annealing system  

3.7. Fe pin dimensions  

3.8. Schematic diagram of the operation mechanisms of a nanoindenter  

3.9. A typical load-displacement curve  

4.1. An example of the surface roughness measured by profilometry  

4.2 (a). Calculated concentration profile of Fe(Cu). (b). Concentration profile from AES for Fe(Cu)  

4.3 (a). Calculated concentration profile of Cu(Fe). (b). Concentration profile from AES for Cu(Fe)
4.4 Calculated concentration profile of Fe(Fe) ........................................ 77
4.5 Calculated concentration profile of Cu(Cu) ........................................ 78
4.6 (a) The Auger survey on Fe(Cu) before sputter cleaning. 
(b) The Auger survey on Cu(Fe) disk before sputter cleaning. .................. 80
4.7 The Auger survey after sputter cleaning of (a) Fe(Cu) disk 
and (b) Cu(Fe) disk ................................................................................. 82
4.8 TEM images and selected area diffraction patterns of the 
Fe(i) disks. ................................................................................................ 86
4.9 An illustration of the structure of the surface layers for 
Fe(i). ........................................................................................................... 91
4.10 TEM photos of the oxides on Fe(Cu) disks ........................................... 91
4.11 Load-displacement curves for (a) Fe(Fe), (b) Fe(Cu), (c) 
Cu(Cu) and (d) Cu(Fe) ............................................................................. 94
4.12 Nanohardness and Young's modulus vs. depth of plastic 
deformation from nanoindentation measurements ................................. 95
4.13 The Fe-Cu phase diagram ................................................................. 100
4.14 An illustration of typical friction traces for Fe/Fe ................................. 102
4.15 Friction coefficient vs. sliding cycles for Cu/Fe and 
Cu/Fe(Cu) under 50 g, 13 mm/sec and 4.5 m sliding 
distance in vacuum ................................................................................. 104
4.16. Friction vs. sliding distance for Cu/Fe and Cu/Fe(Cu) under 50g, 13 mm/sec, 22.5 m sliding distance in vacuum. ................................................................. 105

4.17. Schematic illustration of the friction traces of Cu/Fe(Cu) and Cu/Fe for 2500 sliding cycles under 50g, 13.5 mm/sec, in vacuum. ................................................................. 106

4.18. SEM micrographs of the wear scar on Cu pins of tests on 2500 cycles, 50g and ~13 mm/sec, in vacuum................................................................. 108

4.19. SEM images of Fe(Cu) and Fe disks under 50g, ~13 mm/sec, and 2500 sliding cycles................................................................. 110

4.20. SEM images of wear tracks on (a) Fe disk and (b) Fe(Cu) disk after 2500 cycles of sliding under 30 g load, ~24 mm/sec, in vacuum................................................................. 114

4.21. SEM images of (a) the wear scar on the Cu ball in Cu/Fe(Cu) and (b) wear scar on Cu ball in Cu/Fe, (c) as in (a) but tilted 50° to show the scar roughness, (d) the debris on (b). All the tests here were under 30g, 22~32 mm/sec, 20,000 sliding cycles and in vacuum................................................................. 116

4.22. SEM image of the debris on the Cu ball in Cu/Fe(Cu) as in Fig. 4.5.3 (a), and EDS analysis of the debris, where A, B, C, D correspond to those marked in (a)................................................................. 118

4.23. SEM images and EDS analysis on Cu balls in tests under 30 grams, 23~31 mm/sec, in vacuum................................................................. 122

4.24. SEM images and EDS Fe Kα mapping on the Cu ball in a test with Cu/Fe(Cu) at 30 g, for 45 m, ~24 mm/sec, in 3 x 10⁻⁵ Torr environment................................................................. 125

xiv
4.25. Friction traces for (a) Fe/Fe, (b) Fe/Fe(Fe), (c) Fe/Fe(Cu). All tests were with 30 g load, 12–20 mm/sec, 120 sliding cycles, in vacuum. ................................................................. 127

4.26. SEM images of the wear scars on the Fe pins. All tests were under 30 g, 16–26 rpm, 120 sliding cycles, in vacuum. ................................................. 128

4.27. An illustration of the depth of contact (h) from the Hertzian contact radius a. ................................................................. 131

4.28. Definition of the friction coefficient and error bar. ................... 134

4.29. Types of friction trace. ................................................................... 136

4.30. Friction coefficient vs. sliding distance for tests using Fe pins on Cu(i) disks, at 2.88 g load sliding for 0.45 m in vacuum, sliding speed 15–22 mm/sec. ........................................ 138

4.31. Friction coefficient vs. sliding distance for tests using Cu(Cu) pins on Fe(i) disks, at 2.88 g load sliding for 0.45 m in vacuum, sliding speed 15–22 mm/sec. ........................................ 139

4.32. Friction coefficient vs. sliding distance for tests using Cu(Fe) pins on Fe(i) disks, at 2.88 g load sliding for 0.45 m in vacuum, sliding speed 15–22 mm/sec. ........................................ 140

4.33. Friction coefficient vs. sliding distance for tests using Cu pins on Cu(i) disks, at 2.88 g load sliding for 0.45 m in vacuum, sliding speed 15–22 mm/sec. ........................................ 141

4.34. Friction coefficients vs. sliding distance of Fe/Fe(i) series with 2.88 g load and sliding for 0.45 m, sliding speed 15–22 mm/sec, in vacuum. ................................................................. 143
4.35. Actual friction traces of Fe/Fe(i) series under 10.7g, sliding for 0.45 m in vacuum. ................................................................. 144

4.36. Friction coefficient vs. sliding distance for tests using Fe(Fe) pins on Fe(i) disks, at 2.88 g load sliding for 0.45 m in vacuum, sliding speed 15-22 mm/sec. ................................................................. 145

4.37. Friction coefficient vs. sliding distance for Cu(i) pins sliding on Fe disks at 2.88 g, sliding for 0.45 m, with sliding speed 15-22 mm/sec, in vacuum................................................................. 149

4.38. Surface roughening of Cu(Fe) balls from ion implantation........................................................................................................... 152

4.39. Average friction coefficients vs. disk materials in the order of hardness decrease for tests under 2.88 g, sliding for 0.45 m in vacuum................................................................. 154

4.40. Friction coefficients vs. estimated adhesion energies of the test combinations under 2.88 g load and sliding for 0.45 m in vacuum................................................................. 157

4.41. Friction vs. sliding distance for tests of Fe/Cu with different pin curvatures, at 4.07 g, ~22 mm/sec, in vacuum. ................................................................. 159

4.42. Average friction vs. sliding distance for Fe/Cu with different disk roughness................................................................................. 160

4.43. Plots of friction coefficient vs. sliding cycles for long term tests (a) Fe/Fe(i), Early stage. (a2) Fe/Fe(i), whole range of sliding distance. (b) Fe/Cu(i). All tests are under 2.88 g load, sliding speed is 20-30 mm/sec, in vacuum.......................... 163

4.44. SEM images and EDS Fe mappings of the war scars on the Cu balls of tests with 2.88 g load, <1 sliding cycle (0.034 m), in vacuum. ......................................................................................... 165
4.45. Wear scars and EDS Fe mappings on the Cu balls for tests at 2.88g load, 10 cycles (0.45 m), 20~30 rpm, in vacuum. 169

4.46. SEM images on wear tracks on disks in (a) Cu/Fe(Fe), (b) Cu/Fe(Cu), under 2.88 g load, ~20 mm/sec, 10 cycles, in vacuum. 171

4.47 SEM images and EDS Fe Kα mappings of the war scars on a Cu(Fe) ball of test Cu(Fe)/Fe with 2.88 g load, <1 sliding cycle, sliding speed ~20 mm/sec, in vacuum. 174

4.48 SEM images on wear areas of Cu(Fe) balls in (a) Cu(Fe)/Fe(Cu), (b) Cu(Fe)/Fe(Fe), both under 10.7 g load, and (c) Cu(Fe)/Fe(Cu), (d) Cu(Fe)/Fe(Fe), both under 2.88g load. 175

4.49. SEM images of wear areas on Fe(i) pins of (a) Fe/Fe(Cu), (b) Fe/Fe, (c) Fe/Fe(Fe), with 10.7 g load, 10 sliding cycle, sliding speed ~20 mm/sec, in vacuum. 178

4.50. (a) SEM image of Cu ball in Cu/Cu(Fe), under 2.88g, 10 cycles. (b) Fe Kα mapping of the wear scar in (a). 180

4.51. SEM images of wear scar on Cu balls in (a) Cu/Cu(Fe), (b) Cu/Cu(Cu) and (c) Cu/Cu, with 10.7 g load, 10 sliding cycles, speed 20~30 mm/sec, in vacuum. 181

4.52. SEM images of wear tracks on (a) Cu disk in Cu/Cu and (b) Cu(Fe) disk in Cu/Cu(Fe), under 2.88 g load, ~20 mm/sec, 10 cycles, in vacuum. 183

4.53. A typical wear scar on Cu(Cu) ball, it also shows the surface roughness. In this case, Cu(Cu)/Fe, 2.88 g load, 10 cycles, ~20 mm/sec, in vacuum. 184
4.54. SEM image of the wear scar on Fe(Fe)/Fe(Cu) at different magnifications, under 2.88 g load, ~20 mm/sec, 10 cycles, in vacuum. .......................................................... 185

A1. Microhardness (Hv) vs. load (gf) in hardness tests of (a) Fe and (b) Cu. .......................................................... 193

E.1. SEM image of the wear track on the disks slid with 52100 balls for 2500 cycles.................................................. 202

E.2. SEM image of (a) the wear scar on a 52100 ball slid on Fe disk for 100 cycles and (b) the debris on the ball......................... 203

F.1. A typical wear track on the Fe disk with Si contamination from the environment.................................................. 205
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Selected studies on friction and wear of implanted metals.</td>
</tr>
<tr>
<td>3.1</td>
<td>Material source and hardness, annealing temperature.</td>
</tr>
<tr>
<td>3.2</td>
<td>Chemical polishing of Cu balls.</td>
</tr>
<tr>
<td>3.3</td>
<td>Chemical polishing of Fe pins.</td>
</tr>
<tr>
<td>3.4</td>
<td>Ion implantation parameters.</td>
</tr>
<tr>
<td>3.5</td>
<td>Test conditions.</td>
</tr>
<tr>
<td>4.1.</td>
<td>A summary of the profilometry measurements on the disk surfaces.</td>
</tr>
<tr>
<td>4.2</td>
<td>A summary of the results from modeling and AES of implanted disks.</td>
</tr>
<tr>
<td>4.3</td>
<td>List of the d-spacing and plane index and relative intensities of FeO, FeO2, Fe2O3, Fe3O4, and Fe.</td>
</tr>
<tr>
<td>4.4</td>
<td>Profilometry data of the wear tracks on the disks.</td>
</tr>
<tr>
<td>4.5</td>
<td>Profilometry data on the Fe(i) disks.</td>
</tr>
</tbody>
</table>
4.6 Friction coefficients of tests under 2.88 g load, <1 cycles, ~13 mm/sec, in vacuum ............................................................. 133

4.7 Friction coefficient at 2.88 g for 10 cycles in vacuum, sliding speed 15~22 mm/sec ...................................................... 135

4.8 Average values of friction coefficients for tests (including duplicate tests) at 2.88 g sliding for 0.45 m in vacuum, with sliding speed 15~22 mm/sec, with values of standard deviation ...................................................................... 146

4.9. Comparison of the friction coefficients of self-implanted disks A(A) and pure disks A (reference) when sliding against the same pin or ball material ....................................... 147

4.10. Comparison of friction coefficients between self-implanted disks A(A) (reference) with disks implanted with different species A(B) ........................................................................... 148

E1. Friction coefficients under 50g, 17 rpm and vacuum .................... 200

E2. Wear track depth and width(um) on the discs of tests with 52100 balls, at 50 g load, 17 rpm, in vacuum ........................................... 201
CHAPTER I
INTRODUCTION

1.1 BACKGROUND

Tribology is the science and technology of contacting surfaces in relative motion. It is a wide and complex field which includes lubrication chemistry, fluid dynamics, contact mechanics, surface chemistry, deformation and fracture, etc. Researchers tend to focus on the aspects of tribology which closely relate to their own backgrounds. Studies involving lubricated conditions often focus on the surfaces, surface interactions or adhesion, while those with unlubricated conditions focus on subsurface deformation and fracture. Adhesion and deformation of the contacting surfaces in sliding processes determine the friction behavior. They also influence subsequent steps such as debris formation and structural and chemical changes on and near the contacting surfaces. Adhesion and deformation are often intimately connected in the sliding systems, as shown in theoretical and experimental studies both at the microscopic (1, 2) and macroscopic level (49, 154). The computer simulation of Landman et al. (1) has shown that the adhesion of a Ni tip contacting a Au plate leads to the deformation of the Au plate. A similar effect has been shown in experiments involving a field emission tip (2). Johnson (154) has calculated
the plastic strains in sliding processes using a slip-line field and concluded that the effect of adhesion is to increase the plastic strain in the softer sliding component. Rigney et al. (49, 144) have identified a sequence of events during sliding and suggested that adhesion and deformation affect each part of the sequence. Therefore, the effects of both deformation and adhesion are important in friction and wear, and it is generally difficult to separate them. Understanding more about the contributions of the surface (adhesion) and subsurface (deformation) is crucial to understanding the basic mechanisms of tribological processes.

1.2 OBJECTIVE OF THE STUDY

The original purpose of this study was to investigate the sliding behaviors of ion implanted metals to further understand the relative contributions of the surface and subsurface region to friction and wear.

Copper and iron were chosen to be the testing materials because their surface energies and mechanical properties are different and their sliding friction and wear behaviors have been extensively studied. The ion species in ion implantation were also Cu and Fe. Self implantation (M+ into M) should change the mechanical properties, e.g., hardness, of the near surface materials by changing microstructures and defect contents with little change in the surface chemistry. Implantation with different species should cause similar changes but with changes in surface chemistry as well. Therefore, differences in sliding behavior are expected between unimplanted samples and self-implanted samples. These differences would come from structural changes in the near-surface region due to ion implantation. Differences in
sliding behavior are also expected between self-implanted samples and samples implanted with different species. These differences would come from changes in the surface and near surface chemistry due to ion implantation.

1.3 APPROACH

This study is closely related to those of Chen (3) and Akagaki (4). They have studied sliding behaviors of Fe and Cu using a pin-on-disk set-up with normal loads of 60 g, 80 g, and 500 g. The experimental conditions have been chosen using their studies as references. Low load has been used, because the ion implanted layer is shallow (less than 2000 Å) and higher load would mask the effects of ion implantation. The implanted layers have been characterized using Auger Electron Spectrometry (AES), Transmission Electron Microscopy (TEM), and nanohardness measurements. Sliding tests have been performed for 36 combinations of specimens, namely disks and balls of Fe, Fe(Cu), Fe(Fe), Cu, Cu(Cu), Cu(Fe) respectively, with the ion implantation species in the parentheses. Friction traces have been recorded, the extent of material transfer on the specimens has been examined using EDS, the morphology of the wear tracks has been observed by scanning electron microscopy (SEM) and TEM, and the amount of wear has been measured by profilometry.

Chapter 2 is a review of the literature on friction and wear theories and friction and wear behavior of ion implanted metals. Chapter 3 describes the experimental conditions and procedures used in this study. Chapter 4 contains the results and discussion of the this investigation. A
summary and the conclusions of the present investigation are given in Chapter 5. Suggested future work relating to this study is included in Chapter 6.
CHAPTER II
LITERATURE REVIEW

Friction and wear models based on adhesion and deformation aspects of sliding friction and wear are reviewed, followed by an introduction to ion-implantation techniques and a review of friction and wear of implanted metals.

2.1 GENERAL

Friction involves phenomena observed when two contacting solids are in relative motion. The resistant force in friction process is called the friction force (or sometimes simply friction). The gradual damage produced is called wear. The wear rate is often measured by volume loss or weight loss per sliding distance. Friction and wear are closely related. However, high friction does not necessarily lead to high wear, and vice versa. Wear is more complex than friction, because it also includes debris formation and fracture events (5). In the following sections, sliding friction and wear theories are reviewed, followed by an introduction to ion-implantation techniques and a review of friction and wear of implanted metals.
2.2 FRICTION MODELS

2.2.1 Introduction

When one solid is loaded and brought in contact with another solid, initial contact will be only on the tips of surface asperities. Thus the real contact area is different from the apparent contact area. Recognition of this difference has led to the development of current friction theories.

There are two basic empirical "laws" of friction:

1). Friction is proportional to the normal load.
2). Friction is independent of the apparent area of contact.

Sometimes a third law, which states that friction is independent of the sliding velocity, is included.

These laws are often obeyed, but there are many exceptions. For example, according to Rabinowicz (6), the friction force $F_r$ and the normal load $L$ obey the following relation:

$$F_r = CL^x$$  \[2.1\]

where $C$ is a constant and $x$ is a fraction varying from about 2/3 to 1. The first law of friction is true only when $x = 1$. For very hard materials and very soft materials, $x$ is less than 1, and the first law is not obeyed. Another exception to the first law of friction involves materials with a thin hard oxide surface layer and a soft substrate (pure Cu in this case, as shown in Fig. 2.1) (6, 9). The coefficient of friction is defined as the friction force divided by the normal load. According to the first law of friction, the coefficient of friction should be constant for a combination of sliding materials. In Fig. 2.1, the oxide layers on the surfaces dominate at low load,
giving rise to low friction coefficient, while the substrate properties become important at high load, leading to high friction coefficient.

The second law of friction has not been examined closely, and limited studies support it (9).

The third law of friction should also be applied cautiously. For example, it should be restricted to kinetic friction (finite velocity), not to static friction, which is the resistance to the initiation of motion (zero velocity). It is also not expected to hold when thermal effects or strain rate effects become important (20).

![Figure 2.1](image_url)

Fig. 2.1. Variation of the coefficient of friction with the applied normal load for copper sliding on copper in air, unlubricated (6).

Besides the normal load, the relative contributions of surface and subsurface regions of the sliding components and sliding speed, another factor influencing friction is surface roughness as shown in Fig. 2.2. The friction is high with very smooth surfaces because of the increased real
contact area, but the friction is also high with very rough surfaces because of the interlocking of asperities from both surfaces.

![Graph](image)

Fig. 2.2. Dependence of the friction on the surface roughness (6).

The history of the development of friction theories has been discussed in detail in references 7, 8. It is not the purpose of this section to have a full account of all the proposed theories; rather, the main ideas of each category of theories will be presented. Although there are many early investigations involving surface roughness and asperity interlocking and asperity elastic deformation (5, 9), energy dissipation in frictional processes has rarely been considered. There are two main groups of theories which will be discussed here: one emphasizes the adhesion between contacting surfaces, and the other focuses on the deformation of surface asperities and mechanisms of energy dissipation. Studies of friction on microscopic scales will also be discussed.
2.2.2. Adhesion Theories of Friction

The simple adhesion theory of friction was proposed by Bowden and Tabor (10, 11, 12), based on theories of adhesion and interatomic forces, surface roughness and surface asperity interlocking (13). The expression for friction coefficient is composed of an adhesion term and a plowing (deformation) term as explained in the following. Initial contacts on the tips of surface asperities lead to very high contact pressures. The asperities deform plastically until a certain contact area and pressure are reached. Adhesion over these asperities is so strong that the asperities are cold-welded together and form junctions. In order for these two solids to move relative to each other, the junctions must be sheared apart. Thus adhesion is one contributing factor to friction. If one solid is harder than the other, the surface asperities on the harder material will plough the soft surface, displacing soft asperities. Fig. 2.3 shows the types of contacts. For a conical asperity of semi-angle \( \theta \) (see Fig. 2.3), the plowing term is \( \frac{2}{\pi} \cot \theta \), so the friction coefficient becomes:

\[
\mu = \frac{\tau_0}{p_o} + \frac{2}{\pi} \cot \theta \tag{2.2}
\]

where \( \tau_0 \) and \( p_o \) are the shear stress and yield pressure of the soft material, respectively. For a typical surface, \( \theta \) is less than 5° or 6°, the second term is about 0.05 (8), which is generally small and negligible. The first term is about 0.2 since \( p_o \) is about 5\( \tau_0 \) if work-hardening is ignored (8, 9, 12).
Although the simple adhesion theory offers an explanation for the two laws of friction, the friction coefficient predicted is much lower than those normally found in practice. As indicated in reference 13, there are uncertainties in interpreting $\tau_o$ and $p_o$, because $\tau_o$ could be taken as the shear stress of one of the materials or of the interface. Also, the shear stress $\tau_o$ and the yield pressure $p_o$ are not independent (6, 12).

To account for junction growth, Bowden and Tabor (12) modified their theory by substituting the simple shear stress with combined normal
and shear stresses and by incorporating a yield criterion. They derived the following expression for the friction coefficient for the case of metals with a surface film (12, 14):

\[ \mu = \frac{1}{\left[ \alpha(k^{-2} - 1) \right]^{1/2}} \]  

where \( \alpha \) is a constant and \( k \) is the ratio of the critical shear stress of the contaminating film and that of the bulk material. Fig. 2.4 shows how \( \mu \) changes with \( \alpha \) and \( k \). The modified model shows that the friction coefficient tends to be infinite for chemically clean surfaces (\( k = 1 \)); and the friction coefficient falls to very low values for contaminated surfaces (\( k \) is small).

The above modified adhesion theory is plausible, but the theory is too simple to be useful (13). It is based on the assumption of homogeneous and isotropic materials, whereas the real contact surfaces change chemically (if sliding occurs in air, oxidation can occur on the contacting surfaces; material transfer from one sliding component to the other is often observed) and structurally due to plastic deformation. These can not be accounted for by such limited variables as \( \tau_0 \) and \( p_0 \). The model also fails to consider work hardening (12) and surface roughness effects (15).

2.2.3. Deformation Models of Friction

2.2.3.1 Asperity deformation model

A model on plastic interaction of surface asperities was introduced by Green (16, 17) and extended by Edwards & Halling (14, 18). The main assumption in this model is that the sliding motion is parallel to the
Fig. 2.4. Friction coefficient vs. $k$, the ratio of the critical shear stress of the contaminated film to that of the bulk material, in the modified adhesion theory (12).

surfaces in sliding of macroscopically flat surfaces. In addition, an array of similarly shaped asperities with the same height were assumed. In the Edwards & Halling model, the instantaneous shearing force and normal force from initial contact until the separation of the asperities are calculated, referring to Fig. 2.3 (c). The calculation shows that eq. [2.3] of the modified adhesion theory is only a special case of the formulation in the
Edwards & Halling model. The relationship of $\mu$ vs. $k$ (as defined above) in the Edwards & Halling model is shown in Fig. 2.5 (18).

The Edwards & Halling model incorporated work-hardening effects and predicted junction growth over contacting asperities (18). The model needs modification to account for the complex contact surface and subsurface changes during sliding. Furthermore, a realistic asperity size distribution should also be incorporated.

Challen and Oxley have proposed an asperity deformation model (15), based on the works of Green (16, 17) and Edwards and Halling (18). They used a slip-line field to analyze asperity deformation. Their basic assumptions are: 1) the existence of a plain strain condition on the contacting surfaces (the strain is assumed to be zero in the width direction, perpendicular to the direction of motion and parallel to the contact interface), and 2) the isotropic deformation of the softer material at constant flow stress. The resulting friction coefficient is a function of the hard asperity angle $\alpha$ and interfacial film strength $f$. The hard asperity angle $\alpha$ is the angle between the contacting slope and the sliding direction (shown in Fig. 2.6), which is a measure of surface roughness. The interfacial film strength $f$ is the ratio of film strength to substrate shear stress. The result of the slip-line field analysis is shown in Fig. 2.7. It indicates that friction coefficient ($\mu$) increases with increasing surface roughness ($\alpha$) and increasing film strength ($f$). The predicted value of $\mu$ is close to that of experiments. Note also that as $f \to 1$, $\mu \to \infty$, as predicted in the adhesion theory.

The assumption of a plain strain condition in Challen and Oxley's model is justified for sliding of components with machined marks (18).
However, it may not be applicable for fine polished surfaces. The assumption of constant flow stress fails to consider work-hardening effects and anisotropy of the materials as well.

![Graph](image1)

Fig. 2.5. The friction coefficient vs. $k$ (the ratio of the critical shear stress of the contaminated film to that of the bulk material) by Edwards and Halling (18).

![Diagram](image2)

Fig. 2.6. Contacting geometry and definition of $\alpha$ in Challen and Oxley's model (15).
2.2.3.2. Energy based model of friction

Based on microstructural observation of subsurface materials modified by sliding (19), Rigney and Hirth proposed an energy based model of friction (5). The basic assumption of the original model is that at steady state the microstructures of the subsurface stay statistically constant. Friction work in sliding is equal to plastic work, which dissipates as heat completely at steady state. The original model yields (5):

$$\mu = \frac{\omega t \tau \varepsilon}{L}, \quad [24]$$

where $\omega$ and $t$ are the width and thickness of the highly deformed region, respectively. $\tau$ is the shear stress in the deformed region. $\varepsilon$ is the strain per cycle in that region and $L$ is the normal load. Heilmann and Rigney (20, 21, 22) extended the model so it can account for break-in and strain gradients.

Fig. 2.7. Friction coefficient vs. the angle $\alpha$ and interfacial film strength $f$ in Challen and Oxley's model (15).
Material properties were incorporated via stress and strain relations. For a modified Voce-type shear stress/shear strain relation:

$$\tau = \tau_{\text{max}} (1 - \exp(-cy))^{1/2}$$

[2.5]

where $c$ is a constant, the friction coefficient predicted for one crystalline solid sliding against another is:

$$\mu = \frac{NA}{L} \frac{\tau_{\text{max}}}{\tau_{\text{max}}} F\left(\frac{\tau_f}{\tau_{\text{max}}}ight)$$

[2.6]

where $NA$ is the real area of asperity contact, $L$ is the normal load, $\tau_{\text{max}}$ is the maximum (saturation) shear stress of the softer material, and $\tau_s$ is the average surface flow stress. $F(u)$ depends on the form of the stress/strain relation. For the stress/strain relation in eq. [2.5], $F(u)$ varies with $u$ as shown in Fig. 2.8 (21). It has been shown that the predicted $\mu$ is almost the same as that measured from experiments (21). The model can also be applied to materials with coatings (20, 21).

![Fig. 2.8. F(u) vs. u in the energy-based model (21).](image-url)
The friction coefficient predicted by the energy based model approaches that predicted by the adhesion model at the limiting case when $F(u) \rightarrow 1$, that is, $\mu$ becomes the ratio of shear strength and penetration hardness. However, there is a basic difference between the two models, namely, the adhesion model concentrates on the shear of junctions formed by adhesion while the energy model emphasizes the plastic deformation of the sliding components. Plastic deformation on and below the contacting surfaces, as often observed, is an important issue in understanding sliding friction. The energy based model of friction is an alternative to the more familiar models based on force balance. It has the advantage of being easy to extend, because the energy terms are additive. It also suggests that the temperature gradient on the wear surface is not steep, since heat from plastic work is generated within three dimensions rather than two (5). Environmental effects can also be incorporated via surface film properties.

It is accepted that a friction process is a dissipative process. Thus mechanisms of friction must be able to account for friction energy. As noted in reference 23, plastic deformation is almost inevitable for clean metals. Under light loads where there is no apparent change on the friction surfaces, the subsurface may still undergo plastic deformation, and energy may be dissipated by phonons through atomic vibration.

Rice et al. (24) have extended the energy based model by considering plastic deformation energy as involving contributions from asperity interaction and deformation, debris interaction and plowing, and adhesion at quasi-steady-state. The results of the quantitative calculation (25) suggested that the important factors determining friction are
mechanical properties, surface roughness characteristics, and the size and quantity of entrapped debris, but not adhesion.

2.2.4 Microscopic Friction

With the development of atomic force microscopes (AFM) and scanning tunneling microscopes (STM), it is now possible to measure adhesion force and friction force and record surface images at the atomic scale. There has also been progress in computer simulations recently.

A quantum mechanical calculation for metallic adhesion has been performed by Ferrante & Smith (26). As mentioned in Chapter I, Landman et al. (1) have studied tip-substrate interactions using computer simulation. The result, as shown in Fig. 2.9, has demonstrated the adhesion-induced deformation of both the Ni tip and the Au substrate when the tip approaches the substrate and also during the separation of the tip after contact. This is in agreement with Buckley's adhesion work (27) which involved experiments using Field Ion Microscope (FIM) emitter tips of W and Ir contacting Pt and Au. The FIM image showed transfer of Pt and Au to W, and Au and Pt to Ir. These results indicate that the interfacial strength between two clean metals is stronger than the cohesive strength of one of the two metals. Thus bonds break within the cohesively weaker metal, rather than at the interface, when the tip is separated from the flat. Consequently transfer of the cohesively weaker metal to the cohesively stronger metal occurs. Such a tendency has often been observed (3). Pollock et al. (33) have measured the real contact area of W, Ti and Ir tips (less than 100 nm across) on Fe, Pt and Ti surfaces. Upon sputter cleaning followed by pre-heating of Au and pre-heating of the Ir tip, they
observed a sudden drop in resistance at zero load, which indicated an abrupt and finite contact area. They suggested that the adhesion energy (defined as the energy difference of the contact interface energy and the
original surface energies of the solids) increases with surface cleaning, and
the yield strength decreases through heat treatment. Thus, adhesion
between Au and Ir has induced plastic deformation at zero load. A similar
observation was made for a Ti tip contacting a Ti foil (34), where the
deformation and transfer of material from the Ti tip was suggested from
observation of FIM images. The modeling (1) and the experiments (2, 27,
34) are consistent.

The operating principles of AFM and STM have been described in
references 28, 29. When two solids are brought close to each other, their
electron distributions overlap, and a tunneling current can flow if there is
a potential between the solids. The tunneling current varies exponentially
with the spacing of the solids (30). In STM, the signal is detected through
the tunneling current between the tip and the sample. The AFM is a
combination of the principles of the STM and the stylus profilometer (28).
In AFM, a lever with the tip at one end is used to traverse the sample
surface. Surface forces can be detected by a tunneling current or by optical
interference (29).

Mate et al. (32) have measured the friction force of a W tip sliding
on the basal plane of a graphite surface at low load (< 10^{-4} N). The friction
force curves exhibit the periodicity of the graphite surface. The authors
concluded that atomic friction was indeed measured and the friction
behavior was explained by atomic stick-slip. Kaneko et al. (31) have used
STM to obtain surface topography of magnetic disks. They modified the
STM for adhesion and friction force measurements. The friction force in
dry sliding is higher than that under lubricated condition. At zero load,
they have measured finite friction forces between a 10 \mu m W-tip sliding on
carbon-sputtered magnetic disks. Perhaps the actual normal load in this measurement is the attractive force (adhesion) over the contacting interfaces as suggested by Yoshizama et al. (153). Overney and Meyer (147) have developed friction force microscopy, based on the work of Mate et al. (32). By reflecting a laser beam off the backside of the cantilever supporting the AFM tip, they were able to measure the normal and lateral displacement of the cantilever simultaneously. The normal and lateral (frictional) forces can be determined from the bending and torsional force constants of the cantilever. Burnham et al. (150) have used AFM to measure elastic and plastic behavior and nanohardness via nanoindentation, van der Waals forces and the adhesion of the film and the substrate. The force resolution was 1 nanonewton and the depth resolution was 0.02 nm. These attempts have shown that it is possible to gain more insight on microscopic aspects of adhesion and friction using AFM & STM.

Atomic-scale friction was also measured by Krim et al. (151) using a quartz-crystal microbalance (QCM) which consists of a single crystal of quartz oscillating in transverse shear motion. Au and Ag were evaporated onto the QCM, and the atomic fraction of an adsorbed Kr monolayer on Au and Ag was measured through recordings of the vibration frequency and amplitude. In this case, the normal force is the van der Waals force existing between Kr and Au or Ag surfaces. The measured friction coefficient was on the order of $10^{-9}$.

Johnson, Kendall and Roberts (36) have developed a model for the surface energy effect on the contact size and of the force of adhesion between elastic solids under light load. The model indicates that as the
load approaches zero, the surface force becomes important, and strong adhesion can be observed between clean surfaces. The contact areas are larger than those predicted by Hertz (see 37). As shown in Fig. 2.10, surface forces enlarge the contact area, making the stresses tensile at the edge of the contact and compressive in the center. In the JKR model, the apparent Hertz load \( P_1 \) is given by:

\[
P_1 = P_0 + 3\gamma R P_0 + \sqrt{(6\gamma R P_0 + (3\gamma R)^2)} \tag{2.7}
\]

where \( P_0 \) is the applied load, and \( R \) is given by:

\[
\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}
\]

\( R_1 \) and \( R_2 \) are the curvature of the two contacting spheres. \( \gamma \) is the Dupré energy of adhesion, defined by (35):

\[
\gamma = \gamma_1 + \gamma_2 - \gamma_{12}
\]

where \( \gamma_1 \) and \( \gamma_2 \) are surface energy per unit area of the two contacting materials, and \( \gamma_{12} \) is the interfacial energy.

The contact radius \( a \) is:

\[
a = \frac{R}{K} \left( P_0 + 3\gamma R + \sqrt{(6\gamma R P_0 + (3\gamma R)^2)} \right)^{\frac{1}{3}} \tag{2.8}
\]

where

\[
K = \frac{4}{3\pi(k_1 + k_2)}
\]

\( k_1 \) and \( k_2 \) are the elastic constants of the material of each sphere with:

\[
k_1 = \frac{1 - \nu_1^2}{\pi E_1}, k_2 = \frac{1 - \nu_2^2}{\pi E_2}
\]

where \( \nu \) is the Poisson ratio and \( E \) is the Young's modulus of each material.

As shown in reference 36, the contact radius is finite at zero load and is given by:

\[
a = \frac{1}{R(6\gamma R) / K} \]^{\frac{1}{3}} \tag{2.9}
The condition to separate two spheres (or the pull-off force) is given by:

\[ P_0 = -\frac{3}{2} \gamma n R \]  \[2.10\]

For metals, the deformation produced by attractive surface forces between two contacting solids is small, and can be masked by surface roughness (36). Using mica surfaces in a crossed cylinder geometry as described in reference 23, Homola et al. (38) have shown that the sliding of mica surfaces both in dry air and with a monolayer of calcium stearate is adhesive. The measured friction force vs. load has a very good agreement with the JKR theory. Critical shear stress is also measured in their experiments. It is affected by the interfacial force, the applied load and the elastic deformation.

Pollock et al. (33) have also derived an equation for fully plastic deformation that includes the contribution of surface forces:

\[ P + 2 \pi r \gamma = \pi a^2 H \] \[2.11\]

where \( P \) is the applied load, \( r \) is the radius of the tip before contact, \( a \) is the contact radius, and \( H \) is the hardness of the softer material. The coefficient of friction derived by them for a multi-asperity contact based on macroscopic concepts of plasticity is:

\[ \mu = \frac{\tau_m}{H} \left(1 - \frac{\gamma}{\bar{H} \sigma} \right)^2 - 1 \] \[2.12\]

where \( \tau_m \) is the yield shear strength of the metal, and \( \sigma \) is the standard deviation of asperity heights.
The adhesion effects on friction have been reviewed by Pollock (137).

He gives the equation for friction force as:

\[ F_r = 3\pi R\gamma\mu + \mu P + \mu(6\pi R\gamma P + 9\pi^2 R^2\gamma^2)^{1/2} \]  [2.13]
where $R$ is the reduced curvature (see section 2.2.4), $\gamma$ is the adhesion energy, $P$ is the normal load. Equation [2.13] shows that friction force may be non-linear with load. The effects of adhesion on friction has two aspects: first, surface attraction acts in the normal direction, and it has the same effect as an increase in the normal load. Secondly, as shown by the third term, "the attractive force itself varies with contact area and hence with load"(137). The effect of adhesion is to increase the effective normal load. However, the attractive force will be the same everywhere macroscopically except for variations with details of the contact areas during sliding. Thus adhesion can cause an effective normal load variation which in turn causes variation in the deformation of the sliding materials. This effect is only important at microscopic levels.

2.3 WEAR MODELS

Many wear models have been proposed. Examples are Rosenfield's fracture model (39), Suh's delamination model (40), Quinn's oxidation model (41, 42) and fatigue models (43, 44). Since this study deals with adhesion and deformation changes in the thin ion implanted layers in vacuum, the above mentioned models will not be further described. Only Archard's model and a physical model of wear will be discussed here.

2.3.1 Introduction -- The linear wear equation.

Archard proposed a simple adhesive wear model in 1953 (45). The basic assumptions are those of the adhesion theory of friction. In addition,
the model assumes that the dimension of a typical wear particle is proportional to the size of the asperity contact, that the contact radius of the asperities is \( a \), and the sliding distance of asperities is \( 2a \). Archard then derived a linear wear equation:

\[
\frac{V}{L} = k \frac{W}{H}
\]  \hspace{1cm} [2.14]

where \( V \) is the wear volume, \( L \) is the sliding distance, \( W \) is the normal load, and \( H \) is the hardness of the softer material. The wear coefficient \( k \) is interpreted as the probability of debris formation. Equation [2.14] indicates that the volume loss of a material is proportional to the sliding distance and the normal load and inversely proportional to the material hardness.

Although the Archard model is considered to be a classical model of wear, it has several limitations (13, 45). This model can not explain the transitions in wear behavior where the wear rate changes drastically during different sliding stages. Wear debris normally observed are not hemispherical or lumpy, but they are flakes, cylinders, etc. Recent studies (47, 49) have shown that wear debris are often not produced directly from the bulk sliding materials; rather, they are formed after transferred material has mixed with the host materials and deformed and fractured in the contact interface. In some cases, the wear rate depends on the sliding speed. The only material property incorporated in the Archard model is the hardness of the softer material. Other factors such as hardness ratio of the sliding components (4, 138), surface energy and microstructure should also be considered.
2.3.2 A Physical Model of Wear

Based on the structural and chemical characterization and observation of wear surfaces and subsurfaces (cross-sections), Rigney (46, 47, 49, 50, 51) has proposed a physical model of wear. A sequence of events during sliding processes has been identified. Local contact produces large strain plastic deformation on one or both surfaces. This is evident from observations on and below wear tracks. Transfer from one surface to another occurs commonly. For simple metals, the microstructure of the highly deformed surface layer consists of dislocation cells and subgrains, providing possible sites and paths for crack formation and propagation. The surface layer is often nanocrystalline, consisting of materials from both surfaces. It is similar to the material formed in mechanical alloying. As deformation and transfer proceed, loose debris can be generated. The debris particles have the same microstructures as the mechanically mixed material. The nature of the wear surface and debris and sliding characteristics all depend on the relative hardness of the mechanically mixed layer and the adjacent substrate material.

Though no simple wear equation has been derived from this model, it suggests that the sliding wear process includes several complex phenomena, namely, large local plastic strains, adhesive transfer, mechanical mixing and fracture.

According to Rigney (144), the roles of deformation and adhesion can be summarized as follows: "The sliding components, the mechanically mixed material and trapped debris all undergo plastic deformation. Adhesion influences initial transfer events and the integrity of the mechanically mixed material. It also affects the chemical composition and
the volume fraction of phases in the mixed material and in debris. These in turn affect mechanical properties such as hardness, yield strength, ductility and fracture toughness".

Chen et al. (3, 50, 51) have studied material transfer in Fe, Cu, Mo and Ni systems using a pin/disk sliding system in vacuum. They found that transfer occurs initially as discrete particles and it occurs in both directions. During subsequent sliding, the transferred fragments are deformed and fractured and mixed with some base material. The transfer layer in prolonged sliding is composed of finely mixed materials from both sliding components as well as some pieces of newly transferred fragments. Chen et al. also developed an adhesion theory using a regular solution model based on near-neighbor pair bonding. The adhesion energy of pure metal 1 contacting pure metal 2 is given by:

\[ \gamma_a = \frac{5}{6} (\gamma_1 + \gamma_2) + \frac{5 Z \omega_{12}}{24 S} \]  \[2.15\]

where Z is the coordination number, S is the cross-section area of an atom, and \( \omega_{12} \) is an interaction parameter. The work was based on the previous work of Miedema et al. (52, 53) and others (3, 50). Chen et al. concluded that transfer is from the cohesively weaker material to the cohesively stronger material, which is supported by experimental observations (3, 50, 51). Buckley and Pepper also recognized this tendency for transfer (54, 55).

Glaeser et al. (56) have conducted in situ dry sliding wear experiments in a scanning Auger spectrometer using leaded bronze pins and mild steel disks. Transfer was analyzed by AES. With the presence of oxide and hydrocarbon contamination, transfer of bronze to steel occurred
after 20 cycles of sliding. When the steel surface was sputter cleaned, bronze transfer occurred almost immediately. Buckley and Pepper (as quoted in 57) have performed sliding experiments in UHV using hemispherical riders of Fe, Ni, and Co on disks of W, Ta, Mo and Nb. Using AES, it was found that each of the other metals transferred to W, and Co transferred to each of the other metals. Ni and Fe did not transfer to Ta, Mo and Nb.

Akagaki et al. (4) have studied sliding friction and wear of pure metals in the pin-on-disk geometry in vacuum. It was found that severe wear usually occurred when the hardness ratio between the disk and the pin included values below ~1.0. Mild wear typically occurred when the hardness ratio was above ~1.0. The influence of adhesion energy on specific wear rate of the disks depends on the crystal structure. Increasing the adhesion energy causes less wear for FCC metals (Cu, Ni) and more wear for BCC metals (Fe, Mo). The effects of hardness in the sliding processes have been well reviewed by Rigney (138).

2.4 BASICS OF ION IMPLANTATION IN METALS

The factors determining the concentration profile and structural changes of metals subjected to ion implantation are briefly described.

Ion implantation is a technique in which a solid target is bombarded by energetic ions of a certain element, as illustrated in Fig. 2.11. Studies of the basic aspects of ion implantation have been given in several conference proceedings (59, 60, 64, 68, 69).
There are a number of advantages of ion implantation over other conventional surface modification techniques (58, 59, 60):

1). It is a low temperature process. Neither distortion nor significant dimensional changes are produced. The bulk properties remain the same.

2). The implanted atoms are evenly dispersed as they come to rest in the substrate and no internal interfaces are introduced.

3). The surface composition can be controlled. The formation of surface alloys is independent of solid solubility and diffusivity limits governing conventional alloy formation.

4). A pure beam of ions of any atomic number can be implanted into almost any solid.

5). The process is conducted in vacuum and the result is reproducible.
The main limitations of ion implantation are its shallow depth (less than ~2 μm), its high cost and its line-of-sight character (which means that the ions travel in straight lines and they can not reach surfaces with recess regions).

As an implanted ion slows down and comes to rest in the target material, it makes many violent collisions with lattice atoms, displacing them from their lattice sites. These displaced atoms can in turn displace other atoms, and so on. Thus a cascade of atomic collisions is created. One example is given in reference 87 where the collision cascade with sub-cascades in Au created by a single Au ion implantation at 300 keV has been shown by a TEM micrograph. The formation of a collision cascade leads to a distribution of vacancies, interstitial atoms and other types of lattice disorder in the region around the ion path (62). As the number of ions incident on the crystal increases, the individual disordered regions begin to overlap. This may produce an amorphous region with only short-range crystallographic ordering.

The energetic ions lose their energy in the solid mainly by two mechanisms (58, 62, 115): 1). nuclear collision, or screened Coulomb collision, in which the moving ions collide with the target atoms and transmit their kinetic energy to the target atoms. 2). electronic collision, in which the moving particles excite or eject electrons. In other words, there is interaction between electrons associated with the moving ions and the various electrons (both bound and free) in the solid. Nuclear collision can involve large discrete energy losses and significant angular deflection of the trajectory, and is responsible for lattice disorder. The electronic collision involves much smaller energy losses, negligible deflection and
lattice damage. Nuclear stopping predominates for low energy (E) and high atomic number ions (Z₁), whereas electronic stopping is more important for high E and low Z₁. Thus heavy ions penetrate to much shallower depths than light ions because of nuclear stopping.

The ion range distribution in the substrate is close to Gaussian in shape. It can be approximately described by two parameters, the projected range Rp, which is the projection of the total distance R traveled by the incoming ion along the incident beam direction, and the range spread or range straggling ΔRp. As shown in Fig. 2.12, both Rp and ΔRp are determined by implantation energy E, ion atomic number Z₁, and substrate atomic number Z₂.

Fig. 2.12. The dependence of range Rp and range spread ΔRp on the incident ion energy E, electron number and atomic mass of the ion and the substrate Z₁, M₁, Z₂, M₂ of the ion and the substrate, respectively (62).
The concentration profile is primarily determined by the implantation fluence. However, it is also influenced by several secondary effects in the implantation process.

1) **Sputtering.** At high fluences, some target atoms can acquire sufficient energy from the nuclear collisions near the surface so that they can overcome the surface binding energy and escape from the substrate. The mean number of atoms ejected by each incident ion is called the sputtering ratio, or the sputtering yield or the sputter coefficient (63). The heavier the implanted ions, the higher the sputtering ratio. Sputtering can limit the implantation profile when injection and sputtering balance out. At high dosage, the peak of the concentration profile moves to the surface.

2) **Radiation enhanced diffusion and radiation enhanced segregation.** Radiation enhanced diffusion is caused by the net flow of solute atoms when the interstitial atoms and vacancies created during ion implantation escape the collision cascade. This broadens the concentration profile. One example of the radiation enhanced diffusion is Zn⁺ implantation into Al followed by Ne⁺ irradiation (64). The diffusion coefficient is increased and Ne⁺ ions are found over a depth ~1000 Å deeper than the calculated range for the ions (65). For heavy ions, only a small fraction of the point defects created escape the collision cascade.

Radiation enhanced segregation is the flow of solute atoms resulting from a net flow of point defects when there is a coupling between solute atoms and point defects. This is a flow of point defects from their sources (ion cascade) to their sinks (the surface, or other internal boundaries), which in turn gives a preferential flow of solutes. It locally concentrates
solute, and can result in the depletion or enrichment of elements in the surface region, in the growth of surface layers, and in precipitate formation.

3). Ion Beam Mixing. This is the rearrangement of point defects within the collision cascade and the migration of atoms during the cooling period in the vicinity of the cascade. There are three mechanisms of mixing of atoms: recoil mixing, cascade collisional mixing and thermal spike mixing (60). Recoil mixing is a process where some target atoms recoil far from their initial locations after some high energy collisions between the incident ions and these atoms. Cascade mixing is caused by the random movement of high-order recoils within the collision cascades. Thermal spike mixing is caused by the thermal spike effect in which high energy implantation produces local areas with very high temperature for a minute fraction of a second.

4). Channeling. When the ion beam is aligned with a low index crystallographic direction of a single crystal, the ions can penetrate much deeper into the substrate. In polycrystals, the effect is not significant.

In summary, the depth of implanted ions is a function of the acceleration voltage, the atomic mass of the implanted species and the substrate atoms. The concentration of the implanted layer mainly depends on the implantation fluence. It also depends on secondary effects such as sputtering, radiation enhanced diffusion and segregation, ion beam mixing and channeling.
2.5 FRICTION AND WEAR OF IMPLANTED METALS

The review here will focus on the mechanisms of changes of friction and wear behaviors of implanted metals. The persistence effect will also be discussed.

Ion implantation can influence the physical, chemical and mechanical properties of surfaces. Table 2.1 lists some typical studies of friction and wear of implanted metals. Several mechanisms proposed to account for changes in friction and wear will be discussed in the following sections.

Mechanisms of changes in friction and wear of ion implanted metals

1. Increased Microhardness

Because of the shallow depth of the implanted layer (<0.2 μm), microhardness must be measured under very low load. Wei et al. (70) have reported increased microhardness of Fe and 304 steel implanted with N⁺ and Ar⁺ using 5 mN load (70). Onate et al. (72) also measured a hardness increase of 420 stainless steel implanted by N using 24.5 mN and 49 mN. A similar hardness increase was also reported for combinations of ions and substrates (73).

Nanohardness values of some implanted materials were reported in references 123, 127, 128, 129. The results show that hardness increases for N⁺ implanted Fe at 300 keV up to a dose of 10¹⁷ cm⁻². At higher dose the magnitude of hardness increase is reduced. Little or no hardness change is observed for N⁺ implantation into mechanically polished surfaces of stainless steels with various Cr contents (127). Hardness increase is observed for N⁺ implanted Ti-6Al-4V (128, 129), and for N⁺ implanted Fe
Table 2.1 Selected studies on friction and wear of implanted metals
d=decrease,  i=increase,  0=no change.

<table>
<thead>
<tr>
<th>target material</th>
<th>ion</th>
<th>dosage $10^{17}$/cm$^2$</th>
<th>energy keV</th>
<th>dry or lub.</th>
<th>friction change</th>
<th>wear</th>
<th>mechanism</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>304 stainless steel</td>
<td>N$^+$</td>
<td>4</td>
<td>180</td>
<td>dry</td>
<td>0</td>
<td>d</td>
<td>deformation delayed</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>Ti$^+$</td>
<td>2</td>
<td>50</td>
<td>dry</td>
<td>d</td>
<td>d</td>
<td>smaller wear initially</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N$^+$ + Ti$^+$ dual implnt'n</td>
<td>dual implnt'n</td>
<td>dry</td>
<td>d</td>
<td>d</td>
<td>best wear resistance, vac. carburization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1018 steel</td>
<td>N$^+$</td>
<td>4</td>
<td>180</td>
<td>dry</td>
<td>0</td>
<td>d</td>
<td>eliminate stick-slip</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti$^+$</td>
<td>2</td>
<td>50</td>
<td>dry</td>
<td>d</td>
<td>d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M2 steel</td>
<td>N$^+$</td>
<td>4</td>
<td>180</td>
<td>dry</td>
<td>i</td>
<td>i</td>
<td>deleterious</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti$^+$</td>
<td>2</td>
<td>50</td>
<td>dry</td>
<td>d</td>
<td>d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>B$^+$</td>
<td>3</td>
<td>60</td>
<td>dry</td>
<td>delayed</td>
<td>i</td>
<td></td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>B$^+$ + Ti$^+$</td>
<td>2</td>
<td>150</td>
<td>dry</td>
<td>delayed</td>
<td>i</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-plated Fe</td>
<td>B$^+$ + Ti$^+$ dual implnt'n</td>
<td>dual implnt'n</td>
<td>dry</td>
<td>d</td>
<td>i</td>
<td>i</td>
<td>dual implntn. better, more debris</td>
<td></td>
</tr>
<tr>
<td>52100 steel</td>
<td>Ti$^+$</td>
<td>2–5</td>
<td>50–200</td>
<td>dry</td>
<td>0</td>
<td>d</td>
<td>amorphous</td>
<td>106</td>
</tr>
<tr>
<td>440 ss</td>
<td>Mo$^+$</td>
<td>0.28</td>
<td>400</td>
<td>dry</td>
<td>0</td>
<td>d</td>
<td></td>
<td>61</td>
</tr>
<tr>
<td>Cu</td>
<td>B$^+$</td>
<td>1</td>
<td>40</td>
<td>dry</td>
<td>0</td>
<td>d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>420 ss</td>
<td>N$^+$</td>
<td>–1</td>
<td>90</td>
<td>both</td>
<td>d</td>
<td>d</td>
<td>N bind with Cr</td>
<td>72</td>
</tr>
<tr>
<td>1020 steel</td>
<td>N$^+$</td>
<td>5</td>
<td>90</td>
<td>l</td>
<td>d</td>
<td>d</td>
<td>pin &amp; disk</td>
<td>102</td>
</tr>
<tr>
<td>GCr15 steel</td>
<td>N$^+$</td>
<td>5</td>
<td>90</td>
<td>l</td>
<td>d</td>
<td>d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSL316 steel</td>
<td>N$^+$</td>
<td>5</td>
<td>90</td>
<td>l</td>
<td>d</td>
<td>d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52100 steel</td>
<td>Ti$^+$</td>
<td>5</td>
<td>190</td>
<td>dry</td>
<td>d</td>
<td>d</td>
<td>only in high dose</td>
<td>109</td>
</tr>
</tbody>
</table>
and Cr, respectively (129). Hardness increase is also observed in Ti+ implanted Fe and 52100 steel, but not in N+ implanted 52100 steel.

The hardness increase may come from solid solution strengthening, precipitate formation, or defect formation.

a. Solid solution strengthening

i). Substitutional solid solution strengthening

Ion implantation can produce metastable solid solutions exceeding the equilibrium solubility. One such example is Ag+ implanted into Cu with up to 8 at.% Ag (the equilibrium solubility of Ag in Cu at room temperature is negligible), and the sample exhibits high quality single crystal diffraction patterns (74). Another example is a metastable solid solution of up to 20 at.% Mo in Al produced by ion implantation. This system has less than 0.1 at.% solubility at room temperature (75). Another example is W+ implanted Cu where ~90% of the 10^{16}/cm^{2} implanted W atoms are located on substitutional sites (76).

ii). Interstitial solid solution strengthening

In higher dosage, light element implantation (e.g., N+, C+, B+) into substrates that do not form precipitates or compounds will form interstitial solid solutions. High dosage and high temperature (~400 °C) implantation of N+, C+ into 304 stainless steel has been shown to form interstitial solid solution by X-ray diffraction (7i, 77, 78, 79, 80). Another example is from the study of B+ implanted Cu (81), where the implanted Cu remains as a single crystal. The improved fatigue life in this system is attributed to interstitial solid solution strengthening.
b. Precipitate formation

In most of the application oriented studies, light elements such as N, C or B are implanted into steels, which gives rise to the formation of nitrides, carbides and borides. The same is true for implantation using carbide formers (82) like Ti (83) and Cr, V, Mo, Al (84) (also referring to Table 2.1). Light element implantation gives a deeper implanted layer than heavy element implantation because the sputtering and nuclear collision effects in ion implantation are reduced for light elements (section 2.4). Nitride, carbide or boride formation can account for the increase in microhardness, the change in friction and the reduction in wear. Nitrides from N implantation have been identified by Mössbauer analysis (70) and XPS (72).

Goel et al. (85) have measured hardness increase in Ar implanted Al, and attributed the hardness increase to the formation of solid gas bubbles which developed in the aluminum. Nelson (86) has also studied inert gas implantation which gives rise to gas bubble formation in pure metals at elevated temperatures.

c. Defect formation

Defect formation and defect structures have been studied by many groups using TEM. Merkle et al. (87) have studied defect structures in Au+ implanted Au at 270 keV at dosage of $10^{10}$ to $10^{11}$ /cm$^2$ using TEM and dechannelling of light particle beams. Defects observed are displaced atoms, stacking faults, dislocations and clusters of vacancies and interstitials. Displacement cascades in self-implantation of Ag, Au and Cu have also been studied by Merkle et al. (88). It has been found that self-implantations lead to vacancy loops for Cu+ into Cu (66, 86) and void
formation for He\textsuperscript{+} implantation followed by Al\textsuperscript{+} into Al (67). Dislocations and small clusters are produced for Sb implantation in Al at room temperatures (89). Wilkens (90) reviewed TEM studies on implantations of Au\textsuperscript{+} into Cu and W\textsuperscript{+} into Au. In both cases, dislocation loops from vacancies were observed. Nelson and Mayze (121) have reviewed the formation of dislocations and point defects in ion implantation and discussed the effect of free surfaces. Preece \textit{et al.} (81) implanted B\textsuperscript{+} into single crystal Cu at $10^{17}$/cm$^2$ and 25 keV, and TEM studies showed that after implantation the sample remains as a single crystal. Due to little affinity between B and Cu, there was only a small amount of structural damage. The B implantation in Cu did not change the surface microhardness. Matthews \textit{et al.} (91) have examined cross sections of C implanted single crystal Cu using TEM. They found that damage from implantation consisted of small defect clusters, dislocation loops, and dislocation bands immediately beneath the surface. Dense networks of tangled dislocations were reported (58, 60).

2. Changes in work-hardening behavior

Solute dislocation interaction and dislocation pinning by implanted solute in implanted metals were discussed by Hartley (95). He gave a sequence of solute/dislocation interactions to account for wear reduction. Dearnaley (68) argued that solute dislocation interaction in N\textsuperscript{+} implantation in steels accounts for the improvements in fatigue and wear. Hu \textit{et al.} (96) have performed internal friction measurements, and found that implantation reduces the internal friction. They suggested that solute and dislocation interaction (dislocation pinning) is likely.
3. Effects on Phase Stability

One of the possible mechanisms in wear reduction by N⁺ implantation is that N stabilizes oxide films at the wear surfaces (58, 97). Changes in the tendency of phase transformation in metastable alloys due to N⁺ implantation have been reported (71, 98, 99, 100). Singer et al. (98, 99, 100) and Wilbur et al. (71) have reported that N implantation in 304 stainless steel transformed martensite on the work-hardened surface to austenite, or prevented the transformation from austenite to martensite. Thus the surface was less brittle and more wear resistant.

4. Residual compressive surface stress

Robic et al. (73) have measured the stress induced by ion implantation using a cantilever beam technique. They found that stress increased more slowly than linearly with the dosage. Hardness enhancement was independent of the ion species; it depended on the damage. There was no correlation between stress and hardness. However, Warren et al. (101) have measured the compressive residual stress using X-ray diffraction on Fe surfaces implanted with Co⁺, Mn⁺, Mo⁺, Ni⁺, Nb⁺, Ti⁺, W⁺, Y⁺. They found that an increase in microhardness correlated with an increase in residual stress among these ion species. Hartley (95) suggested that residual surface stress leads to fatigue improvement because crack nucleation and propagation are reduced.

5. Surface chemical affinity changes

Ion implantation can change the chemical affinity or adhesion of the contact surfaces. Cui et al. (102) have mentioned that contact resistance between sliding surfaces was increased after implantation, suggesting a
change in the state of adhesion. Warren et al. (101) have implanted several transition metal ions into pure Fe. They suggested that an increase in cohesive energy of the implanted species accounts for the increase in wear resistance and microhardness and the decrease in initial friction coefficient. Enhanced oxidation behavior of Cu⁺ implanted Cu at $10^{16}$/cm² and 200 keV has been reported (69). Hartley (95) has considered the main mechanism in wear reduction to be the thin oxide on implanted metals acting as a solid lubricant. Goode et al. (103) also attributed changes in pin and disc wear ratio from ion implantation to the alteration of the oxidation behavior of the surfaces by implantation.

6. Amorphization or nanocrystal formation

There are many reports of amorphization on Ti implantation into Fe or steels. Knapp et al. (104) has implanted Ti into pure Fe at 90-190 keV. Their TEM analysis showed that the surface layer is amorphous. They found that C incorporation is essential for amorphization when Ti concentration is below 10 at.%. They also suggested that C was from the hydrocarbons in the vacuum (C getter effect or vacuum carburization). Singer et al. (105, 106, 107, 108, 109) have studied 52100 bearing steel implanted with Ti at $4.6 \times 10^{17}$/cm² and 190 keV. Their Auger line shape analysis indicated that Ti was in the form of titanium carbide in the C rich region. At lower dose, where carbon incorporation is insufficient, friction and wear is increased. Amorphization could be the reason for friction and wear reduction in Ti and Ti+C implantation. Implantation of boron into 440C stainless steel has also been shown to produce an amorphous layer (110).
As seen from Table 2.1, both friction and wear can remain the same or change either way from ion implantation. Hartley (95) discussed friction change from the viewpoint of the adhesion model where the critical shear stress at the interface is changed by implantation. He also reported that Ar⁺ implantation in steels increased friction and hardness (contrary to conventional correlation between friction and hardness), while Kr⁺ implantation in steels did not change friction. Suri et al. (111) have shown that there is an increase in Knoop hardness and decreased wear for B⁺ implanted Cu and Be. The N⁺ or B⁺ implantation into Al had little effect on either μ or wear rate, while N⁺ or B⁺ implantation increased friction in Ti. For stainless steel, N⁺ implantation reduces dynamic friction while B⁺ implantation showed little change in friction. Not all ion implantation leads to improvement in wear. As reported in reference 83, Ni⁺ and Cr⁺ implanted 304 stainless steel does not produce significant improvement in wear. Ti⁺ implantation into Ni-plated Fe has shown an increase in friction and adhesion, leading to an increase in wear (82).

These studies have shown that ion implantation changes friction, perhaps because it changes surface adhesion and hardness and because it forms an amorphous layer or transforms the surface materials. It changes wear because it alters shearing and debris formation and possibly changes the dominant mechanism of wear.

Mechanisms of the persistence effect of implanted metals

In nitriding and low alloy steels with N⁺, C⁺, B⁺ implantation, it has been found that wear improvement persists to several μms after the initial implanted layer (~0.2 μm) has worn away. Persistence effects have been
discussed by Hartley (95), Dearnaley (68), Hirvonen (97) and Cui (102). The following mechanisms have been postulated:

a. atomic migration along dislocation pipes
b. nitrogen inward diffusion during implantation at elevated temperatures.
c. plowing of the original layer beneath the original surface level.
d. transfer of N-containing wear debris between the wear surfaces.

Nitride dissolution and movement inward have been suggested by (95, 68). There were contradicting experimental data as quoted in reference (97). Some found N below the implanted depth and others did not. Hu et al. (96) implanted N⁺ into 1018 steel at 10¹⁷/cm² and 75 keV and observed significant improvement in fatigue and cavitation erosion behaviors. However, they did not detect any migration of N during annealing using nuclear reaction. Using SIMS, Cui et al. (102) have detected N at about 2 μm depth after wear tests on N⁺ implanted carbon steel and Cr bearing steel. Many other studies have suggested that implanted ions do not migrate below the worn surface (98).

Light ions like N⁺ can diffuse inward during ion implantation at high temperatures, forming a thicker nitride layer according to references 77, 79. Wei et al. (70) have implanted N⁺ into Fe and 304 stainless steel, and found that nitrides formed during the implantation process do not break up or diffuse inward. Even in 300°C implantation, interstitial N in Fe was not observed.

Mechanical transfer of N-containing material to further depth than the implanted layer is possible. Wei et al. (70) have used an oscillating
pin-on-disc wear tester to study friction and wear. The disk rotates and the pin oscillates in the radial direction simultaneously. Mechanical transport of implanted species into the material does not occur, because there is no fresh implanted material exposed to the wear track after initial sliding. In case of a fixed pin-on-disc tester, there is always some implanted material exposed at the wear track, especially at the sides of the wear track. Their EDS analysis on different points of the wear track confirmed that it is the wear debris that mechanically carried the N-containing materials to the bottom of the wear track, thus producing long lasting wear reduction. Therefore, it seems that the persistence in wear reduction of implanted steels actually comes from the geometric effect of the wear tests instead of inward diffusion.

There are numerous studies on wear improvement by ion implantation, most of them on steel substrates and/or using light ions. However, studies on metals implanted with metal ions are very limited. Therefore, the current study is important not only from the viewpoint of getting more insight into sliding friction and wear, but also from the perspective of obtaining more data on ion implantation in metals (the Fe and Cu systems).
CHAPTER III
WEAR TEST DEVICES AND EXPERIMENTAL PROCEDURES

The pin-on-disk and ball-on-disk apparatus used in this study are described. Sample preparation procedures and ion implantation parameters used are given in this chapter. Experimental conditions and procedures are described. Characterization techniques of the implanted layer and wear tracks are also presented in this chapter.

3.1 WEAR TEST DEVICES
3.1.1 THE VERTICAL PIN-ON-DISK SYSTEM

Most of the studies on sliding wear by Rigney et al. (4, 47, 51) at The Ohio State University have been performed on a vertical pin-on-disk system. This work started with this system. The apparatus was designed originally by Blau (140) and modified by Sawa (141) and Chen (3). As shown in Fig. 3.1, this apparatus allows loading from the outside of the vacuum chamber by using cone shaped gears. A diffusion pump and a mechanical pump are used to obtain a vacuum level of ~10^{-5} Torr. The sample geometry in the vertical pin-on-disk system is shown in Fig. 3.2.

Preliminary tests were performed with the pin-on-disk setup, but a high silicon content was found on the surface of the test samples by using SEM/EDS. It was found that the silicon contamination was caused by the vacuum grease and/or diffusion pump oil after analysis using AES and
SEM/EDS. Thus, the system was thoroughly cleaned and diffusion oil and vacuum grease not containing silicon were used. All later tests were performed on the horizontal ball-on-disk setup (Fig. 3.3).

Fig. 3.1 The vertical pin/ball-on-disk setup.
Fig. 3.2 Sample geometry in the vertical pin-on-disk system.

3.1.2 HORIZONTAL BALL-ON-DISK IN VACUUM

This system was designed by Nadimpalli (142). It is equipped with a turbo-molecular pump. The original loading arm was made of stainless steel, and the strain gauge backing and the rest of the loading arm were in one piece. Tests with a 30 gram load were performed using this system. For lower load, a new loading arm made of aluminum was designed and built for this study, as shown in Fig. 3.3.

The pivot in the original system is shown in Fig. 3.4 (A), where Teflon washers were used over the center shaft. For accurate loading, the washers were replaced by ball bearings as shown in Fig. 3.4(B). Free motion of the bearing balls depends upon precise fitting.
Fig. 3.3 Modified loading system for low load in the horizontal ball-on-disk system. The loading system is enclosed in the vacuum chamber.
Fig. 3.4 Schematic illustration of the pivot for loading arm. (A) original (B) modified.
3.2 SAMPLE MATERIALS AND SAMPLE PREPARATION

The test materials used for this study are Fe and Cu, as discussed in Chapter I. The sources, purity and microhardness of the materials are listed in Table 3.1.

Table 3.1 The source, microhardness and annealing temperature of the materials used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Purity</th>
<th>Specimen</th>
<th>Microhardness (10 g, 10 sec.)</th>
<th>Annealing Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>MRC</td>
<td>Very</td>
<td>pin</td>
<td>87.6 ± 12.3</td>
<td>600 °C</td>
</tr>
<tr>
<td>Fe</td>
<td>Armco, Vacuum cast</td>
<td>99.97%</td>
<td>disk</td>
<td>77.1 ± 8.0*</td>
<td>600 °C</td>
</tr>
<tr>
<td>Cu</td>
<td>commercial</td>
<td>99.9%</td>
<td>ball</td>
<td>59.9 ± 8.1</td>
<td>400 °C</td>
</tr>
<tr>
<td>Cu</td>
<td>commercial</td>
<td>99.99%</td>
<td>disk</td>
<td>40.7 ± 5.0*</td>
<td>400 °C</td>
</tr>
</tbody>
</table>

* For more data, see appendix A.

Disks of Fe and Cu were machined to dimensions as shown in Fig. 3.5 (a), and Cu pins were machined to dimensions as shown in Fig. 3.5 (b).

Because of the shallow depth of the ion implanted layer, the sample surface must be smooth and stress free. Metallographic polishing and annealing of the samples are required for sample preparation.

3.2.1 PREPARATION OF DISKS

The disks were polished through 120, 240, 400 grit silicon carbide papers (note: 600 grit SiC paper was not used because the SiC particles are
more needle-like at this grit, and they can break and embed in ductile materials, producing deep damage during polishing).

Fig. 3.5 Disk and pin dimensions
After rough polishing, the disks were annealed for one hour at 400 °C for Cu or 600 °C for Fe, and furnace cooled to room temperature. The annealing system, as shown in Fig. 3.6, was built for this study. It consists of two tube furnaces with purging gas of the composition of 5% hydrogen and 95% argon. The first furnace uses copper turnings to further reduce the oxygen content in the purging gas to achieve a bright annealing effect (without oxidation of the samples).

After annealing, all the disks were repolished on 400 grit SiC papers (because of surface relief), and 16 μm, 6 μm, and 1 μm in diamond paste. The Cu discs were further polished with 0.3 μm and 0.05 μm alumina mixed with distilled water in a syntron vibrator. The Fe disks were further hand polished with 0.3 μm and 0.05 μm alumina or 0.05 μm colloidal silica using an automatic Minimet Polisher from Buehler. The syntron vibrator was not suitable for Fe discs because it caused surface relief, where individual grains were polished to a different degree. After each step in polishing, the samples were ultrasonically cleaned in acetone and methanol successively, and blown dry using Dust-off. The surfaces were examined by optical microscopy to ensure that they were clean and free of surface inhomogeneities.
Fig. 3.6 A schematic illustration of the annealing system. Silica gel was used to absorb moisture. The first furnace with Cu turnings reduces the oxygen content in the gas mixture. The tubes in the furnaces were made of quartz.

3.2.2 PREPARATION OF PINS AND BALLS

Pure Cu rods of 3/4" diameter were obtained commercially and machined into rods of 3.2 mm diameter. A pair of the rods was mounted to a flat plate by crystal bond. Two parallel flat surfaces were produced in the axial direction, with one of the flat surfaces polished following the
same procedures used for the discs. They were annealed and cut into 2 mm thick slices by either a wire saw or a spark cutter.

After some preliminary tests with pin-on-disk geometry, it was found that it was difficult to reproduce the contact area and alignment at the load used (50 g). The cylindrical pins were then replaced by balls of 1/4" diameter. The Cu balls were obtained commercially, and cleaned in dilute hydrochloric acid and distilled water. Surface analysis of the Cu balls using optical Microscopy and SEM/EDS revealed SiC embedment in the ball surfaces. Therefore, all the balls were further chemically polished. The chemical solutions and procedures used are given in Table 3.2.

Table 3.2 Chemical polishing of Cu balls

<table>
<thead>
<tr>
<th>Solution</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>55 ml H₃PO₄;</td>
<td>Room temperature or 50 °C-80 °C.</td>
</tr>
<tr>
<td>25 ml acetic acid;</td>
<td>~1 minute</td>
</tr>
<tr>
<td>20 ml HNO₃;</td>
<td>Followed by cleaning in distilled water and then in methanol.</td>
</tr>
<tr>
<td>two droplets of HCl</td>
<td>Repeated until satisfactory surface is obtained.</td>
</tr>
</tbody>
</table>

There was no commercial source for Fe balls. Therefore Fe pins with hemispherical tips were machined. Table 3.3 gives their chemical polishing procedures. Their dimensions are shown in Fig. 3.7.
Table 3.3 Chemical polishing of Fe pins (143).

<table>
<thead>
<tr>
<th>Solution</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 ml HF</td>
<td>Plastic container, room temperature, &lt;1 minute. Wash in succession in H₂O₂, distilled water, ethanol, and blow dry.</td>
</tr>
<tr>
<td>94 ml H₂O₂(30%)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3.7 Fe pin dimensions in inches.

3.2.3 ION IMPLANTATION

Ion implantation was performed on some of the Fe and Cu samples (both disks and pin/balls) with Fe ions and Cu ions, respectively, using a Varian/Extrion implanter, model 350-D, at EG&G Applied Technologies in Miamisburg, Ohio. In the implantation process, pure Fe was evaporated onto a W filament, and Fe was ionized by introducing Cl₂ gas into the system. The Fe ions were separated by a magnetic field. The Cu ions were produced in a similar way. The current density of the ion beam is directly
related to the sample heating (119, 128). For this study, room temperature was maintained during ion implantation. Ion implantation parameters are listed in Table 3.4. High energy implantation was used so that relatively thick implanted layers could be produced. Different energies were used to produce a concentration plateau close to the surface.

Table 3.4 Ion Implantation Parameters

<table>
<thead>
<tr>
<th>Target</th>
<th>Energy</th>
<th>Ion implantation parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe, Cu</td>
<td>high</td>
<td>$2 \times 10^{16} \text{Cu}^+/\text{cm}^2 @ 200 \text{ keV}, \ 3 \times 10^{15} \text{Cu}^+/\text{cm}^2 @ 60 \text{ keV}, \ 3.5 \times 10^{15} \text{Cu}^+/\text{cm}^2 @ 35 \text{ keV}$</td>
</tr>
<tr>
<td>Fe, Cu</td>
<td>low</td>
<td>$2 \times 10^{15} \text{Cu}^+/\text{cm}^2 @ 5 \text{ keV}$.</td>
</tr>
<tr>
<td>Fe, Cu</td>
<td>high</td>
<td>$3.4 \times 10^{16} \text{Fe}^+/\text{cm}^2 @ 200 \text{ keV}, \ 3.0 \times 10^{15} \text{Fe}^+/\text{cm}^2 @ 35 \text{ keV}$</td>
</tr>
<tr>
<td>Fe, Cu</td>
<td>low</td>
<td>$2.2 \times 10^{15} \text{Fe}^+/\text{cm}^2 @ 5 \text{ keV}$</td>
</tr>
</tbody>
</table>

3.3 TEST CONDITIONS AND EXPERIMENTAL PROCEDURES

This study is closely related to the previous studies by Chen (3) and Akagaki (4), where Chen used 60 g and 80 g load, and Akagaki used 500 g. However, the range of applicable loads in this study is restricted by the shallow depth of the ion implanted layer. At high load, the effect of ion implantation may be masked or the implanted layer may wear away too quickly; at low load, factors such as surface roughness, surface contamination and signal to noise ratio, etc., become influential. To establish the proper load, preliminary tests under various loads were conducted, and a 50 g load was chosen for a group of tests with a pin-on-disk geometry. For tests with balls or hemispherical pins in the horizontal
ball-on-disk system, a 30 g load was chosen. For tests using the new loading arm, the load used was 2.88 g.

Sliding speed should also be slow to avoid frictional heating. The chosen speed was about 14 mm/sec with a pin-on-disk set-up. Sliding distances were 4.0 m, 20 m and 100 m with wear track diameters of 12 - 14 mm. For the ball-on-disk geometry, the sliding speed was 12-30 mm/sec. Sliding distances were 0.034m, 0.34m, 4.3 m, 54m and 90 m. All the tests were performed in vacuum of about 2 x 10^{-5} Torr to 6 x 10^{-6} Torr. Test conditions used in this study are summarized in Table 3.5.

Friction coefficients were recorded by a chart recorder, with strain gauges bonded to the loading arm. The strain gauges were in full bridge configuration which gives the maximum signal to noise ratio. After each test, both the disc and the pin (or ball) were kept in desiccators containing silica gel which absorbs moisture.

The sliding test procedures on pin-on-disk geometry are listed in Appendix B. The sliding test procedures on ball-on-disk are listed in Appendix C.

3.4 CHARACTERIZATION OF ION IMPLANTED SAMPLES

3.4.1 AUGER ELECTRON SPECTROMETRY

Auger analysis was performed in the Chemical Analysis Lab at The Ohio State University. The Auger Spectrometer used is a Perkin-Elmer model 550 ESCA/Auger Spectrometer, and the sputter gun of the spectrometer is model 04-303. The electron gun is operated at 3 keV and 20 mA/cm². The Ar⁺ beam was at 2 keV, with a beam current density of 100 µA/cm². The raster size was 0.8 mm x 0.8 mm.
Table 3.5 List of test conditions in the vertical pin-on-disk setup and the horizontal ball-on-disk setup.

<table>
<thead>
<tr>
<th>System</th>
<th>Load (g)</th>
<th>Sliding distance (m)</th>
<th>Sliding speed (mm/s)</th>
<th>Sample combination</th>
<th>Number of tests</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>pin/disk</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vertical</td>
<td>20, 50</td>
<td>45</td>
<td>-14</td>
<td>Fe/Fe</td>
<td>3</td>
<td>Preliminary</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td></td>
<td></td>
<td>Fe/Cu</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60, 80</td>
<td>0.2, 1.3, 6.7, 11.2, 90</td>
<td></td>
<td>Cu/Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.5, 22.5, 112.5</td>
<td></td>
<td>Cu/Fe(Cu)</td>
<td>16</td>
<td>μ, SEM/EDS</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.5, 112.5</td>
<td></td>
<td>52100/Fe</td>
<td>4</td>
<td>reference</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.5, 112.5</td>
<td></td>
<td>Cu/Fe(Cu)</td>
<td>20</td>
<td>Cu balls Si in the system</td>
</tr>
<tr>
<td>ball/disk</td>
<td>30</td>
<td>0.9, 112.5, 900</td>
<td>13-30</td>
<td>Cu/Fe(Cu)</td>
<td>9</td>
<td>μ, friction transition</td>
</tr>
<tr>
<td>horizontal</td>
<td></td>
<td></td>
<td></td>
<td>Fe/Fe(l)</td>
<td>3</td>
<td>SEM Profilometry</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>5.4</td>
<td></td>
<td>Cu/Fe(l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.88</td>
<td>0.034</td>
<td></td>
<td>Cu/Fe(l)</td>
<td>8</td>
<td>μ, SEM/EDS</td>
</tr>
<tr>
<td></td>
<td>2.88</td>
<td>0.45</td>
<td></td>
<td>all 36 combinations with duplicates</td>
<td>78</td>
<td>μ, SEM/EDS</td>
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<tr>
<td></td>
<td></td>
<td>&gt;45</td>
<td></td>
<td>Fe/Fe(l)</td>
<td>12</td>
<td>μ, SEM, friction transition</td>
</tr>
</tbody>
</table>

Sputter cleaning was performed using 2 keV beam over a 9 mm by 9 mm area (current density is 0.8 μA/cm²) before profiling. The time used in sputter cleaning indicates the depth of the contaminated surface layer.

The peaks used in obtaining concentration profiles were 688 ± 25 eV for Fe, and 905 ± 25 eV for Cu. These higher energy peaks were used
because they are less subjected to distortions from magnetic fields and sample charging effects (116).

Auger profiles were obtained by alternating sputtering with data collection. Quantitative analysis was obtained with the standard normalization formalism (116):

\[
\text{Atomic percentage: } c_i = \frac{I_i}{\sum_{i} S_i T_i E_{ml} I_i} \times 100
\]

where \( I \) is the peak-to-peak intensity after a five-point smoothing of the data. \( S \) is the elemental sensitivity factor for the element. \( T \) is the total dwell time per data point. \( E_m \) is the modulation voltage. \( n \) is the number of regions.

Atomic concentration profile is obtained by the formula:

\[
\text{Atomic concentration for element } x = \frac{I_x}{\sum_{i} S_i T_i N_i (V/S)_i I_i} \times 100
\]

where \( N \) is the number of sweeps; \( V/S \) is the energy increments, which is applied to peak data values only.

Concentration profiles at different locations on the samples were obtained. In order to get an accurate value of the implanted depth, profilometer measurements were performed over the sputter craters which were etched by Auger sputtering and are visible under the optical microscope on the profilometer.
3.4.2 TRANSMISSION ELECTRON MICROSCOPY

TEM samples were prepared using a back-thinning method. The basic steps in sample preparation include: 1) a piece of the sample, defined by two planes perpendicular to the sample surface and one plane parallel to the surface, was cut by diamond saw. 2) the sample was attached to a flat piece of metal, facing down, using crystal bond. The back side was polished through 120, 240, 400 grit SiC paper to about 0.2 mm. 3) The sample was heated to about 100 °C and transferred onto a piece of glass which was bonded onto a flat aluminum square (sample facing downward). The slurry disc cutter from South Bay Technology was then used to drill through the glass to get samples of ~3 mm diameter. The drilling was performed with a stainless steel drill and the slurry used was a suspension of silicon carbide in glycerol. 4) These samples were ground on the back using 400 grit paper to about 100 μm thick by using a disk grinder. 5) The samples were then dimpled from the back to about 20~30 μm thick through 6 μm, 3 μm and 1 μm diamond paste using a Gatan dimpler. The depth of the damage from the dimpling was about two to three times the grit size. 6) Finally the samples were ion milled from the back at 6 keV and 0.5 mA with the sample surfaces shielded. The incident beam was at an angle of 17° to 12° to the surface. A laser terminator was helpful in detecting the perforation and retaining enough thin areas.

Before the TEM analysis, the sample surfaces were cleaned by placing the surface upward in the sample holder for ion milling at 2 keV and 2 mA for about 2~5 minutes.

A JEOL 200CX TEM was used to examine the back-thinned samples to study the implanted layer and also some wear tracks.
3.5.3 NANOHARDNESS MEASUREMENTS

Nanohardness measurements were made using a Nanoindentor™ at Conner Peripheral, California. The operating mechanism of the nanoindenter is schematically shown in Fig. 3.8. The position of the indenter (thus the depth of indentation) is determined by a capacitance displacement gauge. The loading force is controlled by varying the current in the loading coil. Positions of indentation are controlled by a computer.

![Fig. 3.8 Schematic diagram of the operating mechanism of the nanoindenter (139).](image)

Each run consisted of ten positions 5 μm apart in a rectangular area with 5 points in a row. The indenter was lowered at a constant rate against suspending springs. The sample surface was identified by detecting a change in the indenter velocity. Each indentation consisted of loading,
holding and unloading. The loading rates used during indentation are 1.5 nm/sec, 6 nm/sec and 18 nm/sec for applied loads of 5 mg, 20 mg and 50 mg, respectively. The correspondence of load with total displacement was recorded. The displacement involved both elastic and plastic displacement. Elastic displacement must be subtracted from the total displacement in determining the hardness.

Fig. 3.9 shows a typical load-displacement curve. Assuming the initial unloading is totally elastic, the plastic displacement is equal to the intercept of the abscissa by fitting a tangent line to the unloading curve at the maximum load (139, 145) and extrapolating to zero load. For a diamond pyramid indenter, the ratio of the depth of indentation \( h \) and the contacting area \( A \) is fixed \( (A = 24.5h^2) \). The contact area can be calculated from the plastic displacement. Hardness is determined by dividing the normal load by the projected area. The Young's modulus can also be determined from the load-displacement curve by the following equations (139):

\[
\frac{dh}{dP} = \frac{1}{2h_p} \left( \frac{p}{24.5} \right)^{\frac{1}{2}} \frac{1}{E_r} \quad [3.3]
\]

\[
\frac{1}{E_r} = \frac{1-v^2}{E} + \frac{1-v_0^2}{E_0} \quad [3.4]
\]

where \( \frac{dh}{dP} \) is the reciprocal of the unloading slope, \( H_p \) is the plastic depth, \( E \) and \( v \) are the Young's modulus and Poisson's ratio for the sample, and \( E_0 \) and \( v_0 \) are the same parameters for the indenter.

Therefore, both nanohardness and Young's modulus can be obtained from nanoindentation measurements.
Fig. 3.9 A typical load-displacement curve. Each measurement involved loading from zero to 5 mg, holding, unloading to zero and then loading to 20 mg and 50 mg as shown. The indentations under the three loads were made at the same spot.
3.5 CHARACTERIZATION AFTER WEAR TESTS

-OPTICAL MICROSCOPY, SEM, EDS, PROFILOMETRY AND HARDNESS MEASUREMENTS

After each wear test, the samples were first examined in an Olympus BO61 optical microscope. Wear scar morphology was observed. The samples were then kept in a desiccator with silica gel.

The wear tracks were examined in an SEM (Hitachi S510, Hitachi 4000), at low working distance and high condenser current, for high resolution. For very shallow wear tracks, a high contrast condition (lower condenser current and low magnification, etc.) was used.

Energy Dispersive Spectroscopy (EDS) mapping was done using a JXA-35 or a JSM-820 instrument. The latter has three options for the detector window: a normal Be window, a thin window and a windowless feature. The latter two make it possible to analyze light elements such as oxygen and carbon. The morphology and EDS analysis on the wear tracks were recorded in the form of Polaroid photographs.

A Talysurf model 3 profilometer was used to measure the wear track depth and width. It has a stylus in the form of a four-sided 90° diamond pyramid with a slightly rounded tip about 2.54 µm wide. The stylus traverses the wear track and its up and down movements are recorded and magnified through electrical circuits. The resolution of the profilometer depends on the size of the stylus. An optical profilometer from Wyko Corporation (in the Tribology Lab in the Mechanical Engineering Department at The Ohio State University) was used to measure surface roughness of the disks. It detects the phase shift from interference between
the reflected and the reference beam. The phase shift is proportional to the asperity height. The vertical resolution is about 1 Å. It is important to point out that the different magnifications in the vertical and horizontal directions give a distorted presentation of the surface.

Microhardness measurements on and off the wear track were performed using a Buehler Micromet II Digital Microhardness Tester with a Vickers indenter, at 10 gram load for 10 seconds.
CHAPTER IV
EXPERIMENTAL RESULTS AND DISCUSSION

This chapter has two parts. The first part contains the results and discussion of the characterization of the implanted layer through TEM, AES and nanoindentation. The second part is composed of the results and discussion of the sliding tests in terms of sliding friction behavior, amount of transfer, amount of wear and wear track morphology.

4.1 CONVENTION: There are 36 combinations of tests in this study, namely disks and pins (balls) of Fe, Fe(Cu), Fe(Fe), Cu, Cu(Fe), Cu(Cu) respectively, with the implanted ion species in the parentheses. Each test combination will be denoted by A/B where A is the pin or the ball and B is the disk.

4.2 CHARACTERIZATION OF THE SAMPLE SURFACES.

Fig 4.1 shows an example of surface profiles measured using a profilometer from Wyko Corporation. The average values of surface roughness for the disks are summarized in Table 4.1. The surface roughness indices are defined as:

\[
\text{Root mean square (RMS)} = \left( \frac{1}{N} \sum_{i=1}^{N} (z_i - \bar{Z})^2 \right)^{1/2}, \tag{4.1}
\]

\[
\text{Average roughness (RA)} = \left( \frac{1}{N} \sum_{i=1}^{N} |z_i - \bar{Z}| \right), \tag{4.2}
\]

66
where $\overline{Z} = \left( \frac{1}{N} \sum_{i=1}^{N} z_i \right)$, $z_i =$ height at point $(x, y)$, $i =$ number of data points in the area measured, and $N =$ number of data points.

The data in Table 4.1 were obtained after the surface tilt and surface curvature have been compensated by the built-in software. The roughness values of Fe and implanted Fe disks did not vary much among themselves, whereas those of the Cu and implanted Cu disks did, as can be seen from Table 4.1. The implanted Cu disks were somewhat scratched against the plastic containers that were used to mail the samples before and after the ion implantation. The surface roughness index depends on the area of the sampling. The smaller the sampling area, the smoother the surface roughness is indicated.

Table 4.1 A summary of the profilometry measurements on the disk surfaces. The values listed are the average of two or more measurements. P-V represents the peak-to-valley distance. For sampling area see Fig. 4.1.

<table>
<thead>
<tr>
<th>index\disk</th>
<th>Cu</th>
<th>Cu(Cu)*</th>
<th>Cu(Fe)</th>
<th>Fe*</th>
<th>Fe(Cu)</th>
<th>Fe(Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS (nm)</td>
<td>77.5</td>
<td>124.5</td>
<td>139.5</td>
<td>17.6</td>
<td>40.6</td>
<td>22.5</td>
</tr>
<tr>
<td>RA (nm)</td>
<td>57.1</td>
<td>91.5</td>
<td>106.5</td>
<td>14.3</td>
<td>27.0</td>
<td>17.65</td>
</tr>
<tr>
<td>P-V (nm)</td>
<td>652.5</td>
<td>1048.5</td>
<td>1044.5</td>
<td>139.0</td>
<td>563.0</td>
<td>200.0</td>
</tr>
</tbody>
</table>

*Note: For a sampling area 16 times smaller than that shown in Fig. 4.1 (that is: 238 x 238 $\mu$m$^2$), the measurements on these disks are:
Cu(Cu): RMS = 16.8 nm, RA = 13.5 nm, P-V = 182.5 nm.
Fe: RMS = 2.54 nm, RA = 2.02 nm, P-V = 23.8 nm.
Fig. 4.1 An example of the surface roughness measured by profilometry, in this case for Cu, prepared by mechanical polishing.
4.3 CHARACTERIZATION OF THE IMPLANTED MATERIALS

4.3.1 The Concentration Profile of the Implanted Layer

The computer modeling of the concentration profiles of the implanted layers was conducted by Oak Ridge National Lab. The principles of the modeling have been discussed in references 113, 114. The model uses the formulation of Ziegler, Biersack and Littmark (115) to calculate the nuclear stopping and electronic stopping powers of energetic ions in a target material (referring to section 2.4). The target is divided into many discreet layers. The sputter coefficient (section 2.4) is chosen by linear extrapolation between that for the initial target material and that for the final mixed substance. The model also includes multiple dose/energy summations.

Fig. 4.2(a) shows the calculated concentration profile for Fe(Cu).

With the knowledge of the peak depth of the implanted layer and the fluence used, one may also estimate the value of the peak concentration of the implanted layer. For example, for implantation of Cu into Fe, one can proceed as follows: If the implanted peak is at 500 Å, for an area of 1 cm², the volume of implantation is: vol = 1 cm² x 500 Å = 0.5 x 10¹⁹ Å³. The lattice parameter for Fe is: a_Fe = 2.866 Å, bcc. The number of Fe atoms per volume is: atom/vol = 2/a_Fe³ = 0.0849 atom/Å³. The total number of Fe atoms in this volume is: Fe atoms = 2/a_Fe³ x vol = 4.25 x 10¹⁷ atoms. The Cu fluence is 2 x 10¹⁶/cm² + 3 x 10¹⁵/cm² + 3.5 x 10¹⁵/cm² = 2.65 x 10¹⁶/cm², then the estimated Cu at.% = \frac{2.65 \times 10^{16}}{2.65 \times 10^{16} + 4.25 \times 10^{17}} = 5.87 \text{ at.\%}.

This estimate ignores sputter effects. The estimate of the peak concentration is in agreement with the results of the modeling.
Auger concentration profiles have been obtained from two Fe(Cu) disks, respectively, and the results of AES profiling from the two samples were consistent. Fig. 4.2 (b) shows an example of the Auger profile on the Fe(Cu) disk. The operating principles of AES have been given in section 3.5.1 in Chapter 3. The system used has a nominal sputtering rate of 100 Å/min according to the Ta_2O_5 standard. In order to calibrate the sputtering rate for the test material, the depth of the Auger sputter crater was measured by a profilometer. Since the roughness of the sample surface was of the same order of magnitude as that of the sputter crater, the profilometer measurements are still approximate. The sputtering rate from the depth measurement is given in Fig. 4.2 (b). As can be seen, the results of AES are in agreement with that from the computer modeling in terms of the maximum concentration and the depth of implantation. The best possible accuracy of AES is 0.1 at.% (116). The error on the atomic concentration from AES is typically ±20% of the measurements (117).

The concentration profile of Cu(Fe) from the computer modeling is shown in Fig. 4.3 (a) and that from AES is shown in Fig. 4.3 (b). In this case, there is a difference between the results from the modeling and that from the AES analysis in terms of the peak concentration and the total depth of implantation. Furthermore, an estimate using lattice parameter and Fe ion fluence gives 8.3 at.% for the peak concentration at 440 Å below the surface and 20.2 at.% at 160 Å underneath the surface. These results of the estimated concentrations were higher than the corresponding values from the modeling and AES measurements when taking the peak depths from the respective curves. This overestimation may be caused by neglecting
the sputter effects. The discrepancy between the modeling and the AES analysis may be caused by the uncertainty of the actual sputtering ratio of Fe in Cu. The sputtering ratio is the number of atoms sputtered by an incident ion (section 2.4). The sputtering ratio is related to the sputtering rate which is the depth of material sputtered away in unit time, but the correlation is complicated. The sputtering rate of a material can be calibrated with a standard material of known composition and of the same structure as the sample. In our case, the sample material is composed of a metastable solid solution of Fe in Cu with radiation defects (referring to Fig. 4.14). Thus, it is difficult to produce such a standard material. Attempts to calibrate the sputtering rate of Fe and Cu were made by vapor deposition of a film of Fe and a film of Cu on mirror blanks with surface roughness of 1/8 Na d line (~300 Å), then sputtering through the films. The resulting sputtering rate for Fe is 78.0 ± 6.1 Å/min, and the sputtering rate for Cu is 139.6 ± 9.6 Å/min. Clearly, Cu has a higher sputtering rate than Fe. This suggests that, on the one hand, the surface would be rich in Fe during ion implantation, and on the other hand, the indicated Fe concentration would also be higher than the actual value during AES sputtering. The sputtering ratio can be measured by Rutherford backscattering spectrometry and by proton induced X-ray emission as in reference 118 for Cu self-implantation. Sputtering ratios of Fe and Cu in the implanted disks were not measured in this study. Nonetheless, the sputtering ratio of an element can vary with the composition during ion implantation (119), whereas the computer modeling assumes a constant sputter ratio for one element (120). Thus, uncertainty of the exact sputter ratio in the modeling can be another factor besides sputtering rate in
contributing to the discrepancy in results from the modeling and AES. Although the peak concentration, the peak depth and the total depth of the implanted layer are different from the modeling and from AES, the amount of Fe in Cu, i.e., the areas under the two curves obtained, are the same.

The concentration profiles from modeling for Fe(Fe) and Cu(Cu) are shown in Fig. 4.4 and Fig. 4.5, respectively. In the case of Cu(Cu), the peak is sharp and very close to the surface. It has a different shape from the other implanted cases.

Table 4.2 summarizes these results in terms of the maximum concentration, the peak depth, and the total depth of the implanted layer (ends at about ~10% of the peak on the curves).
Fig. 4.2 (a) Calculated concentration profile for Fe(Cu). Ion implantation parameters are listed in the table above the curves. Solid lines are for implantation at three different energies. Points represent the net effect of all three implantations.
Fig. 4.2 Continued.

Fig. 4.2 (b) Concentration profile from AES for Fe(Cu). Ion implantation parameters are given in Fig. 4.2 (a). The sputter rate is ~183 Å/min.
Fig. 4.3 (a) Calculated concentration profile for Cu(Fe). Ion implantation parameters are listed in the table above the curves. Solid lines are for implantation at two different energies. Points represent the net effect of both implantations.
Fig. 4.3 Continued.

Fig. 4.3 (b) Concentration profile from AES for Cu(Fe). Ion implantation parameters are given in Fig. 4.3 (a). The sputter rate is ~111Å/min.
<table>
<thead>
<tr>
<th>TARGET</th>
<th>IRON</th>
<th>7.87G</th>
<th>5°</th>
<th>keV</th>
<th>Ion</th>
<th>Dose/cm²</th>
<th>keV</th>
<th>Ion</th>
<th>Dose/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc. Type</td>
<td>Planar, Pearson IV</td>
<td>1</td>
<td>208 Fe-56</td>
<td>3.40e16</td>
<td>6</td>
<td>288 Fe-56</td>
<td>3.40e16</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Peak Data</td>
<td>540a 4.79e21 5.35%</td>
<td>2</td>
<td>35 Fe-56</td>
<td>3.88e15</td>
<td>7</td>
<td>35 Fe-56</td>
<td>3.88e15</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Sput. Loss</td>
<td>Coef=6.22 Tot.= 221a</td>
<td>3</td>
<td>3.59e16/cm²</td>
<td>97.4%</td>
<td>4</td>
<td>3.59e16/cm²</td>
<td>97.4%</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Retn. Dose</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4.4. Calculated concentration profile for Fe(Fe). Ion implantation parameters are listed in the table above the curves. Solid lines are for implantation at two different energies. Points represent the net effect of both implantations.
Fig. 4.5. Calculated concentration profile for Cu(Cu). Ion implantation parameters are listed in the table above the curves. Solid lines are for implantation at three different energies. Points represent the net effect of all three implantations.
Table 4.2. A summary of the results from modeling and AES of implanted disks.

<table>
<thead>
<tr>
<th></th>
<th>Modeling</th>
<th>AES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>max.conc.</td>
<td>peak depth</td>
</tr>
<tr>
<td></td>
<td>at%</td>
<td>Å</td>
</tr>
<tr>
<td>Fe(Cu)</td>
<td>~4.93</td>
<td>340</td>
</tr>
<tr>
<td>Cu(Fe)</td>
<td>~5.02</td>
<td>440</td>
</tr>
<tr>
<td>Fe(Fe)</td>
<td>~5.35</td>
<td>540</td>
</tr>
<tr>
<td>Cu(Cu)</td>
<td>~6.50</td>
<td>120</td>
</tr>
</tbody>
</table>

Surface compositions can be obtained from AES. The Auger survey without sputter cleaning on Fe(Cu) and Cu(Fe) disks are shown in Fig. 4.6. The sample surfaces contained C and O. The Auger surveys after sputter cleaning are shown in Fig. 4.7. The surface contamination on the Fe(Cu) disks was shown to be removed after 30 minutes of sputtering cleaning. Since the nominal sputtering rate is 3 Å/min, the surface contamination on the Fe(Cu) disk is less than 90 Å deep. For the Cu(Fe) disks, the surface contamination was removed after about 10 minutes of sputter cleaning. This indicates that the surface contamination on the Cu(Fe) disks is less than 30 Å deep. These results are consistent in that Fe is more reactive than Cu.
Fig. 4.6 (a) The Auger survey on Fe(Cu) before sputter cleaning.
Fig. 4.6 (b) The Auger survey on Cu(Fe) before sputter cleaning.
Fig. 4.7 (a) The Auger survey on Fe(Cu) after sputter cleaning.
Fig. 4.7 Continued.

Fig. 4.7 (b) The Auger survey on Cu(Fe) after sputter cleaning.
The concentration profile of each implanted disk has been determined by using computer modeling and AES with profilometry measurements. The maximum concentrations of the implanted layers on all the disks range from ~4.0 to ~13 at.%. The depths of the peak concentrations range from 120 to 540 Å, and total depths of the implanted layers range from ~650 to 1200 Å. The surface compositions have also been surveyed. The results indicated that the surface contamination layer is several nanometers deep, which is typical of metal surfaces.

4.3.2 TEM STUDIES OF THE IMPLANTED LAYER.

TEM samples were prepared by a back-thinning method from the plain Fe, Fe(Fe) and Fe(Cu) disks. The bright-field (BF) and dark-field (DF) images with the corresponding selected area diffraction patterns are shown in Fig. 4.8 for (a) Fe(Cu), (b) Fe(Fe) and (c) Fe.

The pure Fe disk showed bending contours and single crystal diffraction patterns (c1) or elongated dots (c2) in the ring patterns. Pure Fe was vacuum cast and annealed after rough polishing (see section 3.3.1) which gave large grains (lateral length is larger than 100 μm). The elongation of the diffraction spots indicates that the sample was still strained, possibly during polishing after annealing. The degree of work-hardening was small because the original large grains remained.

The implanted disks of Fe(Cu) and Fe(Fe) all showed diffraction patterns of superposition of the single crystal patterns (base material) and rings which are identified as shown in the figures. The inner rings were Fe oxides, either Fe₃O₄ and/or γ-Fe₂O₃. Table 4.3 gives the interplanar
distance and relative intensities of Fe₃O₄, γ-Fe₂O₃, γ-Fe and α-Fe. The rings of the two oxides are almost always superimposed.

The Fe rings from the implanted samples showed the degree of grain refinement from ion implantation. This depends on the place of view, as demonstrated in Fig. 4.9. The surface of the samples contained a layer of hydrocarbons and oxides which was less than 50 Å as indicated from AES surface surveys. The implanted layer is next, followed by the original large-grained Fe. Some oxides may have formed on both sides of the sample during the TEM sample preparation steps. Thus, different areas would give different combinations of diffraction patterns. The grain refinement and grain size can be seen in Fig. 4.8 (b), which was obtained from the very edge of the thin areas of an Fe(Fe) sample. From these pictures, the grain diameters of α-Fe observed range from about 0.02 to 0.5 μm.

Dislocation networks were observed on the implanted samples (Fig. 4.8, Fig. 4.9).

The oxides on the sample surface are nanocrystalline as demonstrated in Fig. 4.10. This is typical of both Fe(Fe) and Fe(Cu) disks.

Thus, the results from TEM studies showed that there is grain refinement from ion implantation in Fe(Fe) and Fe(Cu) disks. Dislocation networks were observed. The surface oxides are nanocrystalline.
Fig. 4.8 TEM images and selected area diffraction patterns of the Fe(i) disks. (a1) Fe(Cu), BF, (a2) Fe(Cu), DF, (a3) Fe(Cu), DP double exposure to show the g vector used in imagine (a2). (b1) Fe(Fe), BF, (b2) Fe(Fe), DF, (b3) Fe(Fe), DP double exposure to show the g vector used in imagine (b2). (c1) Fe, DP, (c2) Fe, DP.

* Unless otherwise specified, Camera length = 82 cm for electron diffraction from internal calibration with the Fe spots. Voltage = 200 keV.
Fig. 4.8 Continued.
Fig. 4.8 continued,
Fig. 4.8 Continued.
Table 4.3 List of the d-spacings (Å) and plane indices and relative intensities of Fe₃O₄, γ-Fe₂O₃, γ-Fe, and α-Fe.

<table>
<thead>
<tr>
<th>dhkl</th>
<th>hkl</th>
<th>Name</th>
<th>I/I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.90</td>
<td>110</td>
<td>γ-Fe₂O₃</td>
<td>2</td>
</tr>
<tr>
<td>4.85</td>
<td>111</td>
<td>Fe₃O₄</td>
<td>8</td>
</tr>
<tr>
<td>4.82</td>
<td>111</td>
<td>γ-Fe₂O₃</td>
<td>5</td>
</tr>
<tr>
<td>3.73</td>
<td>210</td>
<td>γ-Fe₂O₃</td>
<td>5</td>
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<td>33</td>
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<td>10</td>
</tr>
<tr>
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<td>533</td>
<td>γ-Fe₂O₃</td>
<td>11</td>
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<tr>
<td>1.268</td>
<td>022</td>
<td>γ-Fe</td>
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</tr>
</tbody>
</table>
Fig. 4.9 An illustration of the structure of the surface layers for Fe(i), thinned from the back (from below in this figure).

Fig. 4.10 TEM photos of the oxides on Fe(Cu) disks, (a) BF, (b) DF, (c) DF, double exposure to show the rings used in forming the DF image.
Fig. 4.10. continued.
4.3.3 NANOHARDNESS MEASUREMENTS

The conventional Vickers indenter is a square-based pyramidal diamond with face angles of 136° (122). The depth of the indentation is \( \sim 0.143d \), where \( d \) is the diagonal of the indentation. For Fe, the Vicker's hardness is \( H_v = 77.1 \) (kg/mm\(^2\)) at 10 g load, 10 seconds. Since \( H_v = \frac{2Lsin(\theta)}{d^2} \), where \( L \) is the test load, the corresponding diagonal of the indentation for a load of 10 g is 15.49 \( \mu \)m, and the depth of indentation is 2.2 \( \mu \)m. Since the typical plastic volume involved in an indentation is 10 times the indentation depth (123), the depth involved in conventional microhardness tests far exceeds the depth of the implanted layer (<1200 Å in this study). Therefore, nanohardness measurements are used in this study.

The operating principles of the nanoindenter and the determination of nanohardness and Young's modulus have been discussed in Chapter 3. Fig. 4.11 shows typical load-displacement curves for the implanted disks. The elastic recovery during unloading after each indentation is shown in the plots.

The nanohardness and Young's modulus and their standard variations vs. the depth of plastic deformation are plotted in Fig. 4.12 (a, b) and (c, d). An increase in nanohardness resulting from the decrease of the applied load has often been observed (123). The values shown in Fig. 4.12 may include this effect. This indenter size effect was attributed to pile-up of the sample materials around the indenter and elastic recovery (123), dislocation processes, surface energy and statistical measurement errors as reviewed in (124). Pethica (127) has measured the nanohardness of
Fig. 4.11. Load-displacement curves for (a) Fe(Fe), (b) Fe(Cu), (c) Cu(Cu) and (d) Cu(Fe). The unloading path was generally not followed by the loading process at the next higher load.
Fig. 4.12. Nanohardness (a, b) and Young's modulus (c, d) vs. depth of plastic deformation, respectively, from nanoindentation measurements. Values are the average of 6 to 8 points. The error bars represent the standard deviation (as defined in Appendix D). The errors of the points in (d) are within the symbols.
Fig. 4.12 continued.

![Graph showing Young's Modulus (GPa) vs. Plastic Displacement (Å)](c)

![Graph showing Young's Modulus (GPa) vs. Plastic Displacement (Å)](d)
electropolished 18/9 steel samples and reported an increase in hardness number near the surface. He suggested that this hardness number increase is due to the indenter size effect.

The depths of plastic deformation are different on different disks under the same load. The values of average hardness indicate that the order of hardness increase is: Cu, Cu(Fe), Cu(Cu), Fe, Fe(Cu), Fe(Fe). However, this may not be true if the scatters of the data are taken into consideration. Hardness increases on the implanted disks were expected because ion implantation introduces point defects and gives rise to metastable solid solutions (referring to the Fe-Cu phase diagram in Fig. 4.13).

As discussed in references 125 and 126, if a value $z$ is a function of $x$ and $y$:

$$z = f(x, y),$$

then

$$H = \alpha P h^{-2} \sigma_i^2 = \sigma_i^2 \left( \frac{\partial z}{\partial x} \right)^2 + \sigma_j^2 \left( \frac{\partial z}{\partial y} \right)^2 + 2\sigma_{ij} \left( \frac{\partial z}{\partial x} \right) \left( \frac{\partial z}{\partial y} \right) + \ldots$$  [43]

where $\sigma_i$ is the standard deviation of $i$ (defined in Appendix D). If $x$ and $y$ are unrelated, then $\sigma \to 0$.

The hardness $H$ is a function of the applied load $P$ and the plastic displacement $h$:

$$H = \alpha P h^{-2}$$  [44]

where $\alpha$ is a proportionality constant. One has:
which leads to

$$\sigma_{H}^{2} = \sigma_{P}^{2} \left( \frac{\partial H}{\partial P} \right)^{2} + \sigma_{h}^{2} \left( \frac{\partial H}{\partial h} \right)^{2}$$  \[4.5\]

For nanoindentation at <20 g load, $\sigma_{P} \to 0$, $\sigma_{h} = \pm 0.04\text{nm}$. If these values and the average hardness, load and plastic displacement are used, the resultant hardness variation is <0.03 for all values of the disks. Thus the error introduced by the instrument resolution is very small.

The cause of the observed scatter in nanohardness could be surface roughness (124), microstructural inhomogeneity, composition variation and patches of contamination (127). The changes in the concentration of the implanted ions with the depth have been shown in AES and computer modeling for the implanted disks. The plastic depths in different trials of the nanohardness indentation would have variations which could be affected by the variation in composition. Therefore the composition variation at different depths in the implanted layers can affect the nanohardness measurements.

On the influence of microstructural features, if one takes the plastic depth as 100 to 800 Å, the indentation area ($A = 24.5\text{h}^{2}$ referring to section 3.5.3) is $A=24.5 \times 10^{-4}$ to $15.68 \times 10^{-2} \text{μm}^{2}$. Assuming that the grains are cubic (Fig. 4.8), the grain size would range from 0.05 to 0.40 μm. From the TEM studies, the grain sizes were found to be in the range of 0.02 to 0.5 μm. Thus the sizes of the indentation and grains are of the same order, and
grain orientation and microstructural features can contribute to the scatter in the nanohardness measurements.

An estimate on the influence of surface roughness on the nanohardness data can be made. Assuming that the uncertainty in plastic depth measurements is $30 \text{ Å} (\sigma_h \to 30 \text{ Å})$, as an example, for nanoindentation on a Fe(Fe) disk at 20 mg load, the uncertainty of the load is very small, so $\sigma_p \to 0$, average nanohardness at this load is $H = 5.02$ GPa, and the plastic displacement is $h = 231.00 \text{Å}$. Using equation [4.6], $\sigma_H = 1.30 \text{ GPa}$. The standard deviation of the hardness measurements is 1.35 GPa. Therefore, surface roughness (referring to Fig. 4.1) could be the main factor in the nanohardness scatter, because the peaks and valleys on the same disk give different plastic displacement.

It is expected that there is a correspondence of nanohardness profiles to the implanted concentration profiles of the implanted layers, as shown in references 128, 129.

The Young's modulus measurements are calculated from the tangent lines to the load-displacement curves (section 3.5.3). From the Young's modulus values ($E$), it is confirmed that the elastic strength of Fe is higher than that of Cu. Among Fe(Fe) and Fe(Cu) and Fe, or among Cu, Cu(Fe) and Cu(Cu), the difference in $E$ is small.

The conventional Vickers hardness number, $H_v$, is in kg/mm$^2$. For bulk Fe samples, $H_v = 77 \text{ kg/mm}^2 = 0.76 \text{ GPa}$ at 10g, 10 seconds. So the hardness magnitudes from microhardness and nanohardness measurements are consistent.

In summary, the scatter in the nanohardness could be caused mainly by surface roughness. In addition, compositional differences at
different depths and microstructural features like grain orientations and grain boundaries could also contribute to the scatter. The values for the Young moduli of the disks did not show distinguishable differences among disks of the same material because of the surface roughness limitation.

![Fe-Cu phase diagram](image)

Fig. 4.13. The Fe-Cu phase diagram (156).
4.4 TESTS ON VERTICAL PIN-ON-DISK GEOMETRY

4.4.1 PRELIMINARY TESTS ON Fe/Fe

The goal of the preliminary tests was to choose the right load for the majority of the tests with implanted samples, based on the previous studies on the Cu and Fe system (3,4).

For tests of Fe/Fe under loads of 20, 50 and 80 grams (~15 mm/sec, 2–5 x 10^{-5} Torr), all the tests produced a wear track on the discs with a width equal to that of the pin after a sliding distance of 45 m. Typical friction traces are illustrated in Fig. 4.14. For tests under 20 g, the friction recordings showed a sudden change from smooth sliding to very noisy sliding. For tests with 80 g, there is no low friction process, and the recordings showed immediate high and noisy friction. For 50 g, there is a short period for low friction before the friction transition. The 50 g load was chosen for the later tests.

4.4.2 PRELIMINARY TESTS OF Cu/Fe AND Fe/Cu

Preliminary tests with pure sample combinations set the reference for tests with implanted samples. The test conditions were: load = 60 g, 80 g, 500 g, sliding distances = 0.7, 1.4, 6.7, 11, 90 m, sliding speed = 15–20 mm/sec, environment: vacuum = 2–5 x 10^{-5} Torr. Test combinations were Cu/Fe and Fe/Cu with pin-on-disk geometry.

The friction traces of Cu/Fe were smooth for all the tests, while those of Fe/Cu were rough at first and became smooth after prolonged sliding. As discussed by Rigney (49), this asymmetry could be caused by thermal effects, relative work hardening rates and chemical properties.
Fig. 4.14 An illustration of typical friction traces for Fe/Fe, (a) 20 g, (b) 50 g, (c) 80 g, sliding speed was ~15 mm/sec, in vacuum.

When only shallow grooves were produced on the disk, no compositional change on the disks could be detected from WDS. When patches were formed on the wear track, compositional changes were detected. The analyzed pin samples showed changes in composition, indicating transfer of material from the disks to the pins. This may be caused by the fast work hardening and continual sliding of the pins in the pin-on-disk geometry. Mutual transfer of Cu and Fe in Cu/Fe and Fe/Cu was found. These results are in agreement with previous studies (1, 2).
4.4.3. TESTS OF Cu/Fe AND Cu/Fe(Cu)

A series of tests on Cu/Fe and Cu/Fe(Cu) combinations were done under the following conditions: load = 50 grams, speed = 13–14 mm/sec, sliding distances = 4.5, 22.5, 112 m, vacuum = $5 \times 10^{-5}$ Torr.

1. Friction

The friction coefficients of Cu/Fe and Cu/Fe(Cu) tests for a sliding distance of 4.5 m are shown in Fig. 4.15. As can be seen, the implanted Fe(Cu) disks showed an increase in friction compared with pure Fe disks when sliding against Cu pins. Two trials were conducted for Cu/Fe and Cu/Fe(Cu), and the friction results are reproducible.
Fig. 4.15 Friction coefficient vs. sliding distance for Cu/Fe and Cu/Fe(Cu) (high energy and low energy implantation) under 50 g, 13 mm/sec and 4.5 m sliding in vacuum. The values here are average values on the friction trace. Representative error bars are included.

The friction coefficients vs. sliding distance for Cu/Fe and Cu/Fe(Cu) after sliding of 22.5 m (at 50 g, 13 mm/sec, vacuum) are shown in Fig. 4.16. The friction of the implanted disks Fe(Cu) is again higher than that of pure Fe disks sliding against Cu pins.
Fig. 4.16. Friction (average) vs. sliding distance for Cu/Fe and Cu/Fe(Cu) (high energy and low energy implantation) under 50 g, 13 mm/sec, 22.5 sliding in vacuum. Representative error bars are included.

For sliding tests after sliding of 112.5 m (50 g, 13 mm/sec, vacuum), the friction of Cu/Fe and Cu/Fe(Cu) is illustrated in Fig. 4.17. The friction of the implanted disk Fe(Cu) (vs. Cu pins) was relatively smooth throughout the sliding tests, and the friction coefficient steadily increased. In contrast, the friction of pure Fe disks (vs. Cu pins) had a transition where the friction coefficient had a pronounced increase and the friction trace became very noisy.
2. Wear morphology

For sliding distances of 4.5 and 22.5 m at 50 g load, the wear rates of the Cu pins in Cu/Fe and Cu/Fe(Cu) systems were similar, but the wear rates of the Fe and Fe(Cu) disks were different. The Fe(Cu) disk has only a few shallow discontinuous grooves, whereas the Fe disk shows more and deeper grooves.

Fig. 4.18 shows the wear morphology of the Cu pins sliding on Fe and Fe(Cu) after 112.5 m sliding. The contact areas on the Cu pins were not
the same. In the Cu/Fe(Cu) system, the Cu pin has rolled up debris which contained silicon (from the environment). In the Cu/Fe system, the Cu pin showed extensive deformation. The top portion in Fig. 4.18 b1 has some silicon content, and the flake-like debris on and beside the wear scar showed very high Fe content (some even pure Fe) from EDS analysis. This is not surprising because transfer of material has been observed in many sliding systems (3).

Fig. 4.19 shows wear tracks on Fe(Cu) and Fe disks after 112.5 m sliding at 50 g load. The wear track on the Fe(Cu) disk consisted of grooves, transferred patches, and rolled-up debris which contains Cu and Si in the white spots in Fig. 4.19 (a2). The wear track of the Fe disk showed typical wear morphology with heavy deformation (grooves) and break-up of the deformed layer for debris generation.
Fig. 4.18. SEM micrographs* of the wear scar on Cu pins of tests Cu/Fe(Cu) and Cu/Fe sliding for 112.5 m at 50 g and ~13 mm/sec, in vacuum. (a1) Cu pin in Cu/Fe(Cu), (a2) higher magnification of (a1) in composition mode (image formed from back scattered electrons only), (b1) Cu in Cu/Fe, (b2) higher magnification of (b1). * Unless specified, SEM micrographs or images means images from secondary electrons.
Fig. 4.18 Continued.
Fig. 4.19 SEM images of Fe(Cu) and Fe disks at 50 g, ~13 mm/sec, and sliding for 112.5 m. (a1) Fe(Cu) in Cu/Fe(Cu), (a2) higher magnification of the debris beside the wear track on Fe(Cu), the zoom magnification is 5 times higher than the original, (b) Fe in Cu/Fe.
This series of tests with 50g and three sliding distances showed that Cu implantation into Fe disks increased the friction compared with Fe disks when slid with Cu pins. In all the cases, the implanted Fe(Cu) disks showed less wear (fewer and shallower groves) than Fe disks.

It was very difficult to align the pins against disks, and the long term tests still showed differences in the contact areas on the pins. Thus some tests with 52100 balls instead of the pins were performed, and the results are summarized in Appendix E. Later in the study, the pin samples were replaced with ball samples.
Initial tests with Cu balls were affected by silicon contamination (for the approaches and solution to the problem, see Appendix F). All later tests were performed with a horizontal ball-on-disk setup which has a clean chamber equipped with a turbo-molecular pump. This eliminated the problem of silicon contamination.
4.5. TESTS WITH HORIZONTAL BALL-ON-DISK GEOMETRY

4.5.1 TESTS AT 30 g LOAD

4.5.1.1 Tests on Cu/Fe and Cu/Fe(Cu)

Using a horizontal ball-on-disk geometry, a series of tests on Cu/Fe and Cu/Fe(Cu) combinations were performed under 30 g load, 22–32 mm/sec, sliding for 0.9, 112.5, 900 m. The vacuum level was 2–5 x 10⁻⁵ Torr.

For short term (0.9 m sliding) tests on Cu/Fe and Cu/Fe(Cu), the friction traces all showed spikes and large variations. The average friction coefficient for Cu/Fe was 0.50–0.66, and that of Cu/Fe(Cu) was 0.60–0.80. Thus only minor friction differences exist between implanted and pure Fe disks.

For tests of 112.5 sliding distance, friction behaviors of pure and implanted disks are similar to those shown in Fig. 4.17. For Cu/Fe tests, a friction transition occurred soon after the sliding began, leading to the onset of extensive wear in a short time. For Cu/Fe(Cu) tests, such a transition did not occur even after sliding of 112.5 m. The friction coefficient of Cu/Fe(Cu) increased steadily and slowly, but remained lower than for Cu/Fe after its transition.

For tests of 900 m sliding, the friction transition for the implanted disk occurred after about 720 m sliding. The friction traces included several alternating quiet and noisy periods before the transition. After the transition, the friction and wear of Fe(Cu) and Fe disks were virtually the same when sliding against Cu balls.
Fig. 4.20 SEM images of wear tracks on (a) Fe disk and (b) Fe(Cu) disk after 112.5 m of sliding under 30 g load, ~24 mm/sec, in vacuum.
The wear tracks on Fe(Cu) and Fe disks after sliding for 112.5 m are shown in Fig. 4.20. The wear on the Fe(Cu) disk showed transferred patches at the sides and some deformation (grooves) at the center of the wear track. This is consistent with the persistent effects discussed in section 2.5. The shape of the sphere makes it possible for both sides of the wear track to incorporate fresh implanted material at a shallower depth than at the center of the wear track. The wear track on the Fe disk after sliding for 112.5 m showed extensive plowing and grooving.

After sliding 900 m, the wear tracks on the Fe and Fe(Cu) disks were typical of samples having extensive wear, similar to that shown in Fig. 4.20 (a). Fig. 4.21 shows the SEM images of the wear scars on Cu balls slid on Fe(Cu) and Fe, respectively. The roughness of the wear scar is evident in 4.21 (c). The wear debris are flake-like particles which often have cracks in them, as shown in 4.21 (d). The SEM image and chemical analysis (EDS) of the debris on an Fe(Cu) disk for the Cu/Fe(Cu) combination are shown in Fig. 4.22. The Cu content in the debris of the Fe(Cu) disk mainly comes from transfer from the Cu ball. Subsequent sliding caused the debris to be further mixed with Fe and Cu in the contact area, and both the size and the shape of the debris changed during sliding. The initial transferred material consists of small and almost pure Cu pieces on the Fe(Cu) disk. This is consistent with the bonding strength argument because Cu is softer than Fe. Chen (3) has shown that transfer commonly involves fragments with dimensions of about 1 μm or larger.
Fig. 4.21 SEM images of (a) the wear scar on the Cu ball in Cu/Fe(Cu) and (b) wear scar on Cu ball in Cu/Fe, (c) as in (a) but tilted 50° to show the scar roughness, (d) the debris on (b). All the tests here were under 30g, 22–32 mm/sec, sliding for 900 m in vacuum.
Fig. 4.21 continued.
Fig. 4.22. SEM image of the debris on the Cu ball in Cu/Fe(Cu) as in Fig. 4.21 (a), and EDS analysis of the debris, where A, B, C, D correspond to those marked in (a). A and B were analyzed using area mode, and C and D in point mode.
Fig. 4.22 continued.
To check the reproducibility of the friction behavior in Cu/Fe(Cu) at long sliding distances (~900 m), additional tests were performed under 30 g load. It was found that the time in the low friction stage before the transition varies from test to test for the Cu/Fe(Cu) combination. Initially it took 720 m sliding to reach the transition. Later, there were tests in which 315 m and 90 m sliding were enough to reach the transition. To add to the confusion, one test in the Cu/Fe system also demonstrated this friction behavior and the transition occurred after sliding for 405 m. One test with Cu/Fe(Fe) was also performed and the transition occurred around 13.5 m sliding distance. Thus, the transition in the friction trace is not restricted to Cu/Fe(Cu), although most of the tests on this combination showed longer pre-transition periods than Cu/Fe and Cu/Fe(Fe). Perhaps, whenever the transfer of Fe to the Cu balls reaches such a degree as to make the sliding of Cu/Fe(i) similar to the self-mated case with Fe/Fe(i), a transition in friction occurs.

SEM images with EDS mapping of Fe Kα on the Cu balls for tests at 30g are shown in Fig. 4.23. It is seen that the areas of the wear scars are about the same, though the critical number of sliding cycles varies. The degree and the uniformity of transfer are different. In order to examine the characteristics of the friction transition, an additional test was conducted with Cu/Fe(Cu) at 30 g, ~24 mm/sec, for ~45m sliding in vacuum. The test was stopped during the quiet period of friction recording. The wear track on the Fe(Cu) disk consists of incomplete circles, thin and shallow. Fig. 4.24 shows the SEM images of the wear scar on the Cu ball and EDS Fe Kα mapping. The area of wear scar is comparable with those shown in Fig. 4.23. The transfer was rather uniform. Perhaps the low friction in the pre-
transition region depends on the initial local contact characteristics (sample surface roughness, curvature, chemistry) and the degree and uniformity of the transfer.

Table 4.4 lists the data from profilometry measurements on the wear tracks on the disks. It indicates that the amount of wear varies in the order of Cu/Fe < Cu/Fe(Fe) < Cu/Fe(Cu).

Table 4.4 Profilometry data (average of three or more measurements) of the wear tracks on the disks. All tests were performed under 30 g, 18~27 mm/sec, in vacuum.

<table>
<thead>
<tr>
<th>tests</th>
<th>sliding cycles</th>
<th>average width of wear track (µm)</th>
<th>average depth of wear track (µm)</th>
<th>width * depth sliding cycles after friction transition</th>
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</thead>
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<tr>
<td>Cu/Fe</td>
<td>20819</td>
<td>887.5</td>
<td>23.5</td>
<td>1.81</td>
</tr>
<tr>
<td>Cu/Fe(Cu)</td>
<td>7840</td>
<td>825.0</td>
<td>15.8</td>
<td>29.6</td>
</tr>
<tr>
<td>Cu/Fe(Fe)</td>
<td>500</td>
<td>808.0</td>
<td>12.1</td>
<td>19.9</td>
</tr>
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</table>
Fig. 4.23. SEM images and EDS analysis on Cu balls in tests under 30 grams, 23–31 mm/sec, in vacuum. (a1) SEM of the wear scar on the Cu ball in Cu/Fe, sliding for 936.8 m, and (a2) Fe mapping of (a1). (b1) SEM on Cu ball in Cu/Fe(Cu), sliding for 352.8 m, and (b2) Fe mapping of (b1). (c1) SEM of Cu ball in Cu/Fe(Fe), sliding for 22.5 m, and (c2) Fe mapping of (c1).
Fig. 4.23 Continued,

(b1)

(b2)
Fig. 4.23 continued.
Fig. 4.24. SEM images and EDS Fe Ka mapping on the Cu ball in a test with Cu/Fe(Cu) at 30 g, for 45 m, -24 mm/sec, in 3x10^{-5} Torr environment. (a). SEM image of the wear scar on the Cu ball. (b) SEM image of part of the wear scar at higher magnification. (c) EDS mapping of the area in (b).
4.5.1.2 Test of Fe/Fe(i) under 30 gram load

Tests of Fe/Fe, Fe/Fe(Cu) and Fe/Fe(Fe) were done under the following conditions: 30 g load, 12-20 mm/sec, 5.4 m sliding. The friction traces are shown in Fig. 4.25. It can be seen that the lengths of the initial friction period were different and that the initial friction coefficients vary
as follows: Fe/Fe(Fe) (0.33–0.4) < Fe/Fe(Cu) (0.47) < Fe/Fe (0.73). The implanted disks have lower initial friction than the pure Fe disk does.

Fig. 4.26 shows the SEM images of the wear areas on the Fe pins. The wear scar of the Fe pin in Fe/Fe(Cu) is larger than for the other cases. The morphologies near the centers of the three pins are similar. An example is shown in Fig. 4.26 (d). Table 4.5 lists the profilometry data from the disks. The amount of wear changes in the order Fe/Fe < Fe/Fe(Fe) < Fe/Fe(Cu), whereas the wear track depth varies in the opposite order. Thus, these tests with Fe pins on Fe(i) disks show that implanted disks give lower initial friction and shallower wear tracks, but larger wear volume.
Fig. 4.26 SEM images of the wear scars on the Fe pins, (a) Fe pin in Fe/Fe, (b) Fe pin in Fe/Fe(Fe), (c) Fe pin in Fe/Fe(Cu), (d) the details of the wear morphology in the center, in this case, on Fe pin as in Fe/Fe(Fe). All tests were under 30 g, 16–26 rpm, sliding for 5.4 m in vacuum.
Fig. 4.26 continued.
Table 4.5 Profilometry data (in μm) (average over 4 measurements) on the Fe(i) disks. Tests were done at 30g load, 12~20 mm/sec, sliding for 5.4 m in vacuum.

<table>
<thead>
<tr>
<th>Test</th>
<th>width (μm)</th>
<th>depth (μm)</th>
<th>area (w * d)</th>
</tr>
</thead>
<tbody>
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<td>218.75</td>
<td>6.60</td>
<td>1443.75</td>
</tr>
<tr>
<td>Fe/Fe(Fe)</td>
<td>430.00</td>
<td>5.30</td>
<td>2279.00</td>
</tr>
<tr>
<td>Fe/Fe(Cu)</td>
<td>637.50</td>
<td>4.95</td>
<td>3155.60</td>
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</table>

4.5.1.3 THE DEPTH OF DEFORMATION VS. THE NORMAL LOAD.

Hertz's theory of elastic contact can be used to estimate the initial contact area and the depth of elastic deformation. Alternatively, equation [2.8] in chapter 2 from JKR (36) can also be used, by taking surface effects into consideration.

From reference 37, the Hertz contact radius is:

\[ a = \left( \frac{3PR}{4E^*} \right)^{\frac{1}{3}} \]  

where \( P \) is the applied load, \( R \) is defined as \( \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \), \( R_1 \) and \( R_2 \) are the curvatures of the two contact surfaces. In the case of a ball on a disk, \( R = \) ball radius. \( E^* \) is defined as \( \frac{1}{E^*} = \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2} \), where \( E_1 \) and \( E_2 \) are the Young's moduli of the two solids, and \( v_1 \) and \( v_2 \) are the Poisson's ratios of the two solids.

From reference 132, \( E_{Cu} = 125 \) GPa, \( E_{Fe} = 208.2 \) GPa. \( v_{Cu} = 0.343, v_{Fe} = 0.291. \) \( R = 0.25" = 6.35 \) mm. Thus, the contact radius under 30 g load is: \( a = 25.5 \) μm. The depth of this contact (see Fig. 4.27 below) is: \( h = R - \sqrt{R^2 - a^2} \). Thus \( h = 516 \) Å at 30g.
The depth of plastic deformation after sliding begins is larger than the estimate from elastic contact. Since the thickness of the implanted layer was about 1000 Å for the disks, lowering the load may make it easier to study the effect of implantation on friction and wear. Thus, a new loading arm which allows tests at low load (> 2 g) was built. Appendix G gives the derivation of the relationship of friction force and the thickness of the strain gauge backing beam. Tests under 2.88 g were performed following the above tests. Under this load, the calculated Hertz contact radius is $a = 11.55 \ \mu m$, and $h = 105 \ \AA$. 

Fig. 4.27 An illustration of the depth of contact (h) from the Hertz contact radius a.
4.5.2 TESTS AT 2.88 g LOAD

Using the new test system with ball bearings at the pivot point of the loading arm, sliding tests with 2.88 g load were performed for sliding distances: ~0.034 m (<1 cycle), 0.45 m (10 cycles), 54 m (1200 cycles) and 90 m (2000 cycles). For some tests of Cu/Fe(i), sliding was stopped immediately after the friction transition. The friction behaviors of materials in these tests are discussed first, followed by the discussions on the extent of material transfer and on the wear scar morphologies.

4.5.2A Friction

4.5.2.A1. Short term tests (<1 cycle)

The short term tests were performed to examine the initial friction and the extent of transfer.

The friction coefficients of the tests are listed in Table 4.6. Fig. 4.28 shows how the friction coefficients were determined from the recording trace. Duplicate tests were performed for some of the combinations, and the results were consistent in terms of friction coefficient. Cu/Fe showed the lowest friction (0.23). Ion implantation of the disks increased friction as in Cu/Fe(Fe) (0.65, or 0.76) and Cu/Fe(Cu) (0.65~0.76). Between Cu ion and Fe ion implantation into Fe disks, there was not much difference in friction. Cu/Cu(Fe) gave slightly lower friction than Cu/Cu. The implantation of the balls increases friction in the case of Cu(Cu)/Fe (0.4~0.88) compared with Cu/Fe (0.23). Thus, implanting the disks as in Cu/Fe(Fe) and Cu/Fe(Cu) or implanting the balls as in Cu(Cu)/Fe leads to an increase in friction compared with the pure samples under the same
test conditions. However, there was no significant increase in friction when the Cu disk was implanted with Fe.

It should be noted that these tests were done consecutively within 3 days to make the test conditions the same for each test as much as possible. The friction in the initial transient period is difficult to reproduce, because it is influenced by many parameters as will be discussed in section 4.5.2.A2.1. The absolute value of friction may vary in these combinations, but the trend in friction change in each subgroup of disks or pins of A, A(A) and A(B) should remain the same under the same conditions.

Table 4.6 Friction coefficients of tests under 2.88 g load, 0.034 m, ~13 mm/sec, in vacuum. A comma separates \( \mu \) from two tests. Reading uncertainty is \( \Delta \mu = 0.02 \).

<table>
<thead>
<tr>
<th>ball\disk</th>
<th>Fe</th>
<th>Fe(Fe)</th>
<th>Fe(Cu)</th>
<th>Cu</th>
<th>Cu(Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.23, 0.65--0.76</td>
<td>0.65, 0.31--0.43</td>
<td>0.29--0.35</td>
<td>0.31--0.43</td>
<td>0.29--0.35</td>
</tr>
<tr>
<td>Cu(Cu)</td>
<td>0.23--0.35</td>
<td>0.40--0.59</td>
<td>0.65--0.88, 0.40--0.59</td>
<td>0.76</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 4.28 The determination of friction coefficient from the friction trace. Error bars used in later figures are defined by the difference between the min. and max. as shown here.

4.5.2.A.2 Tests for 10 cycles (0.34 m)

While the short term tests in section 4.5.2.A.1 give information on the extent of initial transfer (referring to section 4.5.2.B), longer term tests (at 0.34 m) provide a more stable friction reading and more transfer information as well.

The friction coefficients for all 36 combinations are listed in Table 4.7. These tests were performed with 2.88 g load, sliding for 0.45 m, 15~22 mm/sec, under $5 \times 10^{-5} \sim 9 \times 10^{-6}$ Torr, for one trial in each combination. Tests in each subgroup (defined as disks of A, A(A) and A(B) vs. same pin material) in these tests were performed consecutively within one or two days to make the test conditions the same throughout. The determination of friction coefficient and notation for the sliding characteristics are defined in Fig. 4.29.
Table 4.7 Friction coefficients of tests for one trial at 2.88 g for 10 cycles (0.45 m) in vacuum, with sliding speed 15~22 mm/sec. Reading uncertainty is $\Delta \mu = 0.02$.

For definition of sliding characteristics, referring to Fig. 4.29. $R_o =$ rough, $R_1 =$ rough + spikes, $S =$ smooth, $S + S =$ smooth with spikes.

<table>
<thead>
<tr>
<th>Disk</th>
<th>Fe</th>
<th>Fe(Fe)</th>
<th>Fe(Cu)</th>
<th>Cu</th>
<th>Cu(Cu)</th>
<th>Cu(Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.36-0.48</td>
<td>0.37-0.49</td>
<td>0.54-0.58*</td>
<td>0.76-0.88^</td>
<td>0.41</td>
<td>0.41</td>
</tr>
</tbody>
</table>
| S        | $R_1$ | $R_1$ | $S$    | $S$ | $S + S$ | $S + S$
| Fe(Fe)   | 0.49-0.55 | 0.55-0.65 | 0.29  | 0.35 | 0.38   | 0.17-0.39 |
| $R_o$    | $R_o$ | $R_o$ | $S + S$ | $S$ | $S$    |
| Fe(Cu)   | 0.53-0.67 | 0.51-0.63 | 0.25-0.32 | 0.38-0.48 | 0.38-0.46 | 0.29-0.41 |
| $R_o$    | $R_o$ | $S$    | $R_o$  | $S + S$ | $S + S$ |
| Cu       | 0.15-0.25 | 0.82-0.94 | 0.65-0.88 | 0.53-0.76 | 0.41   | 0.51-0.75 |
| $R_o$    | $R_o$ | $S$    | $R_o$  | $S + S$ | $R_1$
| Cu(Cu)   | 0.27-0.53 | 0.3-0.33 | 0.48-0.52 | 0.70-0.86 | 0.36-0.42 | 0.43-0.49 |
| $R_1$    | $R_o$ | $R_1$ | $R_o$  | $R_o$  | $R_1$
| Cu(Fe)   | 0.76-0.97 | 0.17-0.30 | 0.38  | 0.52-0.62 | 0.31   | 0.40-0.50 |
| $R_1$    | $R_o$ | $S$    | $R_o$  | $R_o$  | $S$

* See Fig. 4.31 and statements on that page.
^ See Fig. 4.33A and associated discussion.
Fig. 4.29 Types of friction traces. $S$ = Smooth, $S+S$ = Smooth + Spikes, $R_o$ = Rough, $R_1$ = Rough + Spikes.

From Table 4.7, one has the following observations:

1. The friction coefficients obtained for sliding of 0.034 m and those for 0.45 m were consistent and basically reproducible.

2. For the combinations of Cu/Fe and Cu/Fe(Cu), there is consistency of tests performed under different conditions. With pin-on-disk sliding at 50g load for 4.5 m and 22.5 m (section 4.4.3), and with ball-on-disk sliding at 2.88g load for 0.034 m and 0.45 m, the friction results on Cu/Fe and Cu/Fe(Cu) all indicated that the friction coefficients of Cu/Fe were lower than those of Cu/Fe(Cu). In this combination the effect of ion implantation was to increase friction. When comparing tests of Cu/Fe(Fe)
with Cu/Fe, it is seen that the self-implanted disks also gave an increase in friction at 2.88 g load, sliding for 0.034 and 0.45 m.

3. There is a consistency of friction trends between Fe(Fe)/all disks and Fe(Cu)/all disks, Cu(Cu)/all disks and Cu(Fe)/all disks, respectively. When Cu pins were used, the friction of Fe disks was lower than that of implanted Fe disks. When Cu(Fe) pins were used, the friction of Fe disks was higher than that of the implanted Fe disks.

Effects of disk implantation can be examined by comparing the friction data horizontally in Table 4.7; while effects of pin implantation can be examined by comparing the friction data vertically. These effects will be discussed following the discussion on the duplicate tests (section 4.5.2A.2.1). Attempts to reproduce the results in Table 4.7 have been made on some of the subgroups (with disks of A, A(A) and A(B) sliding with different pins). Each duplicated subgroup will be discussed separately.

1. For the Fe/Cu(i) series, plots of the friction coefficient vs. sliding distance for the Fe/Cu(i) series are shown in Fig. 4.30. The Fe/Cu combination gave the highest level of friction among the tests in Fe/Cu, Fe/Cu(Cu) and Fe/Cu(Fe). The implanted disks of Cu(Cu) and Cu(Fe) gave similar low values of friction coefficients, except one test of Fe/Cu(Cu) (Cu(Cu) disk #3 in Fig. 4.30). The exceptional high friction in this test of Fe/Cu(Cu) is possibly caused by the scratches after ion implantation on the Cu(Cu) disk surface. The scratches caused more unimplanted bulk material to be exposed during sliding, leading to high friction similar to that of the pure Cu disk. The increased surface roughness can cause an increase in the number of contacting asperities, also leading to increased
Fig. 4.30. Friction coefficients vs. sliding distance for tests using Fe pins on Cu(i) disks, at 2.88 g load sliding for 0.45 m in vacuum, sliding speed 15-22 mm/sec. Representative error bars are given.
friction (referring to Fig. 2.2). Other factors affecting friction, as will be discussed in section 4.5.2A.2.1, may also contribute to the exceptionally high friction in this combination.

2. For the Cu(Cu)/Fe(i) series, two duplicate tests were done as shown in Fig. 4.31. The differences in friction among the three kinds of disks are not pronounced. The Fe(Fe) disks showed slightly lower friction than the other disks.

Fig. 4.31 Friction coefficient vs. sliding distance for tests using Cu(Cu) pins on Fe(i) disks, at 2.88 g load for sliding 0.45 m in vacuum, sliding speed 15~22 mm/sec. Representative error bars are given.
3. For the Cu(Fe)/Fe(i) series, the results on friction are shown in Fig. 4.32. Fe disks give the highest friction, and Fe(Fe) and Fe(Cu) have lower friction with self-implanted Fe(Fe) disks having the lowest friction among the three kinds of disks.

![Friction coefficient vs. sliding distance for tests using Cu(Fe) pins on Fe(i) disks.](image)

**Fig. 4.32.** Friction coefficient vs. sliding distance for tests using Cu(Fe) pins on Fe(i) disks, at 2.88 g load sliding for 0.45 m in vacuum, sliding speed 15-22 mm/sec. Representative error bars are given.

* Tests were under 10.7 grams with all other parameters being the same.
4. For the Cu/Cu(i) series, duplicate tests were done using 10.7 g load. The results are shown in Fig. 4.33. Cu(Fe) disks have higher friction than Cu(Cu) disks. The friction of Cu disks varies between tests using the two loads (2.88 g, 10.7 g).

Fig. 4.33. Friction coefficient vs. sliding distance for tests using Cu pins on Cu(i) disks, at 2.88 g load sliding for 0.45 m in vacuum, sliding speed 15–22 mm/sec. Representative error bars are given. Hollow symbols represent tests at 2.88 g, and shaded symbols represent tests at 10.7 g with all other parameters being the same.
5. For the Fe/Fe(i) series, Fig. 4.34 shows the friction traces of all the tests with 2.88g load and sliding for 0.45 m. The friction of Fe/Fe is fairly reproducible, but the friction data for Fe/Fe(Cu) fall into two groups. One is higher (0.56, 0.53) than for Fe/Fe and the other is lower (∼0.38). For Fe/Fe(Fe), two tests showed a similar level of friction, while the third one gives a lower value. There is no clear difference in friction between Fe/Fe and Fe/Fe(Fe), while the friction values of Fe/Fe(Cu) vary slightly around the average friction for Fe/Fe or Fe/Fe(Fe).

Three tests were done with 10.7g load (Hertz contact radius $a=15.96$ μm, depth of elastic deformation over contact is $h=200$ Å) to further check the friction in this series. The friction traces are shown in Fig. 4.35. The trace for Fe/Fe(Cu) included large spikes. The friction coefficient is 0.29–0.30 for Fe/Fe, 0.28–0.31 for Fe/Fe(Fe), and 0.24–0.28 for Fe/Fe(Fe). Thus Fe/Fe and Fe/Fe(Fe) have similar friction levels, and Fe/Fe(Cu) has slightly lower friction. This is in agreement with some of the previous tests shown in Fig. 4.34 (e.g., Fe disk #1, #2, #3, Fe(Fe) disk #1, #2 and Fe(Cu) disk #1, #4).
Fig. 4.34. Friction coefficients vs. sliding distance of Fe/Fe(i) series with 2.88 g load, sliding for 0.45 m, sliding speed 15–22 mm/sec in vacuum. Representative error bars are given.
Fig. 4.35. Actual friction traces of Fe/Fe(i) series under 10.7g, sliding for 0.45 m in vacuum.
6. For the Fe(Fe)/Fe(i) series, the results are shown in Fig. 4.36. Fe(Fe)/Fe(Cu) has lower friction than Fe(Fe)/Fe. The reproducibility with Fe(Fe)/Fe(Fe) is not as good as for the other tests.

In summary, sliding friction tests on the 36 combinations with duplicate tests have been performed, sometimes under higher loads (4.07 or 10.7 g). Although friction during the run-in period is influenced by many factors, results on some subgroups have shown that the friction levels can be reproduced. The average values of friction coefficients for
tests on the 36 combinations are listed in Table 4.8 with the standard deviation by including the duplicate tests under 2.88 g load. Upon detailed examination of the friction traces, it is found that the friction behavior can vary from test to test for the same combination, e.g., for Fe(Fe)/Fe, one test showed smooth sliding while another trial showed rough sliding (referring to Fig. 4.34). This is related to the local surface roughness and composition. A summary on friction of the 36 combinations will be given after the following discussion.

Table 4.8 Average values of friction coefficients for tests (including duplicate tests) at 2.88 g sliding for 0.45 m in vacuum, with sliding speed 15–22 mm/sec, with values of standard deviation.

<table>
<thead>
<tr>
<th>Disk</th>
<th>Fe</th>
<th>Fe(Fe)</th>
<th>Fe(Cu)</th>
<th>Cu</th>
<th>Cu(Cu)</th>
<th>Cu(Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.47 ± 0.06</td>
<td>0.38 ± 0.12</td>
<td>0.44 ± 0.11</td>
<td>0.39 ± 0.18</td>
<td>0.43 ± 0.12</td>
<td>0.52 ± 0.16</td>
</tr>
<tr>
<td>Fe(Fe)</td>
<td>0.47 ± 0.04</td>
<td>0.41 ± 0.16</td>
<td>0.27 ± 0.03</td>
<td>0.35 ± 0.01</td>
<td>0.38 ± 0.01</td>
<td>0.29 ± 0.03</td>
</tr>
<tr>
<td>Fe(Cu)</td>
<td>0.60 ± 0.09</td>
<td>0.58 ± 0.05</td>
<td>0.29 ± 0.04</td>
<td>0.40 ± 0.05</td>
<td>0.46 ± 0.06</td>
<td>0.28 ± 0.05</td>
</tr>
<tr>
<td>Cu</td>
<td>0.22 ± 0.01</td>
<td>0.90 ± 0.08</td>
<td>0.71 ± 0.06</td>
<td>0.63 ± 0.05</td>
<td>0.40 ± 0.01</td>
<td>0.62 ± 0.07</td>
</tr>
<tr>
<td>Cu(Cu)</td>
<td>0.54 ± 0.09</td>
<td>0.44 ± 0.09</td>
<td>0.51 ± 0.06</td>
<td>0.78 ± 0.09</td>
<td>0.40 ± 0.03</td>
<td>0.44 ± 0.01</td>
</tr>
<tr>
<td>Cu(Fe)</td>
<td>0.72 ± 0.13</td>
<td>0.34 ± 0.10</td>
<td>0.49 ± 0.13</td>
<td>0.57 ± 0.08</td>
<td>0.31 ± 0.01</td>
<td>0.46 ± 0.03</td>
</tr>
</tbody>
</table>

4.5.2.A.2.1 Discussion of friction

The original expectation of the study was that differences in sliding behavior between the unimplanted samples and the self-implanted samples would come from the structural changes in the near surface region due to ion implantation, and differences in sliding behavior
between the self-implanted samples and the samples implanted with
different species would come from the surface chemistry changes due to
ion implantation. As discussed later, this is not simple, because of the
various factors influencing friction for the experimental conditions used in
this study. Nevertheless, comparisons should be attempted.

The comparison of the friction coefficients of self-implanted disks
A(A) and pure disks A (reference) when sliding against the same pin or
ball material is given in Table 4.9. It shows that the friction coefficients of
self-implanted disks were decreased for the combinations of Cu(Cu)/Fe(Fe),
Cu(Fe)/Fe(Fe), Fe/Cu(Cu), Cu(Cu)/Cu(Cu), and Cu(Fe)/Cu(Cu) compared
to those of pure disks under the same condition. The friction coefficients
of the self-implanted disks were not changed significantly for the
combinations of Fe/Fe(Fe), Fe(Fe)/Fe(Fe), Fe(Cu)/Fe(Fe), Fe(Fe)/Cu(Cu),
Fe(Cu)/Cu(Cu), Cu/Cu(Cu), compared with the friction coefficients of the
pure disks under the same condition. The friction coefficient of the self­
implanted disk was increased for Cu/Fe(Fe) compared with that for Cu/Fe.

Table 4.9. Comparison of the friction coefficients of self-implanted disks
A(A) and pure disks A (reference) when sliding against the same pin or
ball material.

<table>
<thead>
<tr>
<th>pin\disk</th>
<th>Fe and Fe(Fe)</th>
<th>Cu and Cu(Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>~</td>
<td>&gt;</td>
</tr>
<tr>
<td>Fe(Fe)</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>Fe(Cu)</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;</td>
<td>~</td>
</tr>
<tr>
<td>Cu(Cu)</td>
<td>&gt; or ~</td>
<td>&gt;</td>
</tr>
<tr>
<td>Cu(Fe)</td>
<td>&gt;</td>
<td>&gt;</td>
</tr>
</tbody>
</table>
Table 4.10 gives the comparison of friction coefficients between self-implanted disks A(A) (reference) with disks implanted with different species A(B). The friction coefficients for the Fe(Cu) disks were decreased using Fe(Fe) and Fe(Cu) pins, compared with those for the Fe(Fe) disks under the same conditions, except for one test of Fe(Fe)/Fe(Fe) (#3 in Fig. 4.35). However, the friction coefficients for the Fe(Cu) disks were increased using Cu(Cu) and Cu(Fe) pins, compared with those for the Fe(Fe) disks under the same conditions, except for one test of Cu(Cu)/Fe(Fe) which gives similar friction values for Cu(Cu)/Fe(Cu) (#2 in Fig. 4.30). Similarly, the friction coefficients for Cu(Fe) disks were decreased using Fe(Fe) and Fe(Cu) pins, compared with those for the Cu(Cu) disks under the same conditions. However, the friction coefficients for Cu(Fe) disks were increased using Cu, Cu(Cu) or Cu(Fe) pins, compared with those for the Cu(Cu) disks under the same conditions.

Table 4.10. Comparison of friction coefficients between self-implanted disks A(A) (reference) with disks implanted with different species A(B).

<table>
<thead>
<tr>
<th>pin\disk</th>
<th>Fe(Fe) vs. Fe(Cu)</th>
<th>Cu(Cu) vs. Cu(Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>&gt; or &lt;</td>
<td>=</td>
</tr>
<tr>
<td>Fe(Fe)</td>
<td>&gt;</td>
<td>&gt;</td>
</tr>
<tr>
<td>Fe(Cu)</td>
<td>&gt;</td>
<td>&gt;</td>
</tr>
<tr>
<td>Cu</td>
<td>= or &gt;</td>
<td>&lt;</td>
</tr>
<tr>
<td>Cu(Cu)</td>
<td>&lt; or =</td>
<td>&lt;</td>
</tr>
<tr>
<td>Cu(Fe)</td>
<td>&lt;</td>
<td>&lt;</td>
</tr>
</tbody>
</table>
Similar comparisons can be made between different pins/balls sliding with the same disk materials. An example is shown in Fig. 4.37 for the combination of Fe disks and Cu(i) balls, the friction coefficient for Cu/Fe is low, while friction coefficients for Cu(Fe)/Fe and Cu(Cu)/Fe are high. In Table 4.8, Cu/Fe(Cu) and Cu/Fe(Fe) showed high friction, whereas Cu(Cu)/Fe(Cu), Cu(Fe)/Fe(Cu), Cu(Cu)/Fe(Fe) and Cu(Fe)/Fe(Fe) all showed low friction.

![Friction coefficient vs. sliding distance for Cu(i) pins sliding on Fe disks at 2.88 g, sliding for 0.45 m, with sliding speed 15~22 mm/sec, in vacuum. Representative error bars are given.](image)

**Fig. 4.37.** Friction coefficient vs. sliding distance for Cu(i) pins sliding on Fe disks at 2.88 g, sliding for 0.45 m, with sliding speed 15~22 mm/sec, in vacuum. Representative error bars are given.
1. Factors affecting the friction coefficient:

From the above discussion, it is seen that the changes in friction caused by ion implantation are rather complex. As discussed in reference 133, one difficulty associated with understanding friction is the inability to observe what is happening at the interface during sliding. "It is incredible that, all properties being known (surface energy, elastic properties, loss properties) a friction coefficient cannot be found by an a priori calculation" (35). Many questions about friction remain unanswered, particularly events in the very beginning of sliding. This inevitably leads one to considerations of surface roughness, surface structure and surface chemistry, especially at low normal load.

1. Surface chemistry and surface roughness.

As reviewed in Chapter 1, clean metal surfaces tend to give very high friction, while the effect of oxides on the surface is thought to lower the friction and to alter the adhesion energy. From our AES surveys and TEM studies, the surface layer with oxides is a few nm thick. This may still influence friction at the load level used in this study.

Surface roughness can be characterized by profilometry, but the information content and adequacy of the surface roughness indices, like RMS, RA (as defined in section 4.2), have been questioned (134, 135, 136). These commonly used indices can not give information about the details of the surface. A more thorough statistical treatment would be an option (136). There may be sharp tips on some of the surface asperities which would give friction at the atomic scale. As discussed in chapter 2 and by
Pollock (137), the adhesion energy becomes important when the contact curvature is:

\[ R \leq 48\pi\gamma / \kappa \]  

where \( \gamma \) is the Dupre energy (defined in section 2.2.4), and \( K \) is the elastic constant as defined in section 2.2.4. To make an estimate, take \( \gamma \) as

\[ \gamma = 0.85(\gamma_1 + \gamma_2) - \gamma_{chem} \]  

where \( \gamma_1 \) and \( \gamma_2 \) are the surface energies of the two metals, and \( \gamma_{chem} \) is the contribution from chemical interaction of the atoms of the two metals (52).

According to Miedema (155), the surface energy of a solid metal at \( T = 0 \) K is about 1.13 times of the surface energy of the liquid metal which is measured. The surface energy of a solid metal at temperature \( T \) is given by:

\[ (\gamma V_m^{2/3})_T = (\gamma V_m^{2/3})_0 + bT \]  

where \( V_m \) is the molar volume of metal \( m \), and \( b = -0.49 \times 10^{-7} \) J/K. The estimated surface energies at room temperature from the measured surface energies of liquids for Fe and Cu are 2.5 and 1.8 J/m\(^2\), respectively (155). The value \( \gamma_{chem} \) for Fe-Cu is 0.4 J/m\(^2\) (53). Thus \( \gamma = 3.2 \) J/m\(^2\) for the Fe-Cu system. Referring to section 4.5.1.3, we have \( K = 154 \) GPa and \( R = 35 \) Å. On the real surface, it is possible that some local curvature would be of this order of magnitude (Fig. 4.1). Thus, the effects of surface roughness at the nanometer scale may determine the magnitude of adhesion-induced plastic deformation. As discussed later, this causes the normal load to vary, thus affecting the friction coefficient at the atomic scale. However,
this effect may be negligible in this study, because the loads used (> 2.88 g) was comparatively high.

Surface roughness also influence the real contact area $A_r$, which in turn affects friction ($F_r = \tau A_r$).

An example of surface roughening from ion implantation on the Cu(Fe) balls is shown in Fig. 4.37. This is caused by non-uniform sputtering during ion implantation (119).

Fig. 4.38. Surface roughening of Cu(Fe) balls from ion implantation.
Any scratches produced after ion implantation and before the sliding test may cause friction increases (referring to discussion of the Fe/Cu(i) series), especially at short sliding distances. The local roughness in the real contact area influences the contact pressure, and changes in roughness alter the subsequent material response during sliding.

2. Nanohardness of the surfaces, hardness gradient near the surface and relative hardness ratio between the disk and the pin.

Hardness characterizes a material's resistance to deformation. It is one of the material properties which is included in most friction and wear models. It is related to a material's yield strength (130) by a constant: \( H = cY \), where \( c \) is 2.6 for Tresca's yield criterion and \( c = 3 \) for von Mises' yield criterion. Hardness affects the plastic deformation of the materials in sliding. An increase in the surface hardness can also lead to an increase in the shear strength of the material, thus decreasing junction growth and lowering the friction, according to adhesion models.

As discussed in section 4.3.3, the nanohardness measurements indicate that the order of hardness increase for the disks is Cu, Cu(Fe), Cu(Cu), Fe, Fe(Cu) and Fe(Fe), based on the average nanohardness values. Fig. 4. 39 plots the friction coefficients vs. disk materials in the order of hardness decrease for the tests under 2.88 g load sliding for 0.45 m in vacuum. The decreased friction of the implanted disks compared with the unimplanted disks sliding against Fe, Cu(Cu), Cu(Fe) pins is due to the hardness increase from ion implantation (because of grain refinement and defect formation).
Fig. 4.39. Average friction coefficients vs. disk materials in the order of hardness decrease for tests under 2.88 g, sliding for 0.45 m in vacuum.

Hardness profiles can be calculated from the load-displacement curves provided that the calibration of the true indentation area vs. plastic depth is known (139). The areas of indentation were measured by TEM carbon replica in (139). Such a calibration has not been done for the present measurements. However, studies of nanohardness in N implanted ARMCO iron and N⁺ implanted Ti-6Al-4V (129, 128) indicate that nanohardness profiles correspond to the implantation concentration
profiles (i.e., Fig. 1 and Fig. 2 in (129), Fig. 2 and Fig. 7 in (128)). The decreased friction of Fe(Fe) relative to Fe in the tests with Cu(Cu)/Fe(Fe) and Cu(Fe)/Fe(Fe) balls may be related to the hardening of Fe(Fe).

Friction can also depend on the hardness ratio of the pin and disk (4). When the initial hardness ratio of disk to pin is below \( \sim 1.0 \), a transition in friction occurs shortly after sliding started; when the initial ratio is greater than \( \sim 1.0 \), long sliding distances are needed to reach the transition in friction. For friction in the transient period, individual local events, including local hardness ratio, may be more important than the overall properties in the steady state. If one examines Table 4.8, one can see a pattern in the friction values. For example, Fe/Cu (\( \text{Hd/Hp} < 1 \)) has high friction (0.76–0.88), while Cu/Fe (\( \text{Hd/Hp} > 1 \)) has low friction (0.15–0.25). However, the hardness ratio argument does not seem to be in agreement with the test combinations involving implanted materials, because the combinations of Fe(Fe)/Cu (\( \text{Hd/Hp} < 1 \)) and Fe(Cu)/Cu (\( \text{Hd/Hp} < 1 \)) have lower friction than Fe/Cu, while Cu/Fe(Fe) (\( \text{Hd/Hp} > 1 \)) and Cu/Fe(Cu) (\( \text{Hd/Hp} > 1 \)) have higher friction than Cu/Fe.

3. Change in Adhesion energy due to ion implantation

The changes in adhesion energy by ion implantation can be estimated using eq. [4.9]. Assume that the surface energy changes linearly with the concentration of the implanted species. The surface energy of Fe(Cu) is 2.465 J/m\(^2\), and for Cu(Fe) it is 1.835 J/m\(^2\), taking the concentration of the implanted species as 5 at.%. Using eq. [4.9], the adhesion energy ranges from 4.25 for Fe/Fe to 3.06 for Cu/Cu. Fig. 4.40 plots the friction coefficients vs. the estimated adhesion energies of the test
combinations under 2.88 g load and sliding for 0.45 m in vacuum. The friction coefficients do not correlate well with the adhesion energy changes.

Rabinowicz (48) has used adhesion energy to explain the friction behavior of carbon-coated glass-based rigid magnetic disks sliding against a composite pin (70% aluminum oxide and 30% titanium oxide). Adhesion leads to transfer which in turn changes adhesion. A reduction of adhesion energy by implantation of N into Ti has been reported (34).

4. Variation of the sliding speed

The main effect of sliding speed is to change the rate of heating of the surfaces. The reason for speed variation in this study is that the motor was run near its lower limit. Thus the speed is not even. However, at the low speed used, frictional heating is small (146), and it is unlikely that our friction values were influenced by these variations.

From the above discussion, it is seen that the dependence of friction on parameters such as load, materials involved, local properties and local events, and their changes with time should be considered. For most of the test combinations, hardness increases of the disks from ion implantation lead to lower friction compared with the unimplanted disks. Adhesion effects caused by ion implantation of Cu ions into Fe and Fe ions into Cu can not be clearly separated from the effects of the above mentioned factors.
Fig. 4.40 The friction coefficients vs. the estimated adhesion energies of the test combinations under 2.88 g load and sliding for 0.45 m in vacuum.
2. Possible experimental errors

The possible source of experimental errors could be curvature variation of the pins, friction at the pivot point and variation in surface roughness of the surface of the disks.

The pins were machined into a hemispherical tip. After the chemical polishing, uneven curvature was observed on some of the pins. However, the contact radius was very small compared with the radius of the pin. Also, pins with similar curvatures were chosen for tests in each subgroup. It is unlikely that the friction trend in the series was modified by variation in the curvature of the pins. Nonetheless, the effect of curvature variation on the pins should be checked. Fig. 4.41 shows the results of Fe/Cu with Fe pins of maximum differences in curvature among all the Fe pins. The maximum effect of the curvature variation on friction, Δμ, is about 0.15.

As to the effect of friction in the pivot point, one can proceed as follows. The friction coefficient is defined as the friction force Fr divided by the normal force L. That is, μ = Fr/L. When L1 = L + dL where dL denotes the effective load due to joint friction (dL can be positive or negative), the actual friction force is: Fr1 = μ(L + dL). Thus, the friction coefficient reading is μ1 = μ(1 + dL/L). The error in the friction coefficient resulting from uncertainty in the exact normal load is μ x (dL/L). In each test, the maximum value for dL is less than 0.5 g, which can unbalance the loading arm. Thus, the error in μ is less than 17% at 2.88 g; it is less than 12% at 4.07 g; it is less than 5% at 10.7 g. Increasing the normal load reduces the effect of friction in the pivot point (that is why some tests were
performed at load of 4.07 g and 10.7 g in the duplicate tests), but high load may mask the effect of the ion implantation.

![Graph showing friction vs. sliding distance for tests of Fe/Cu at 4.07 g, ~22 mm/sec, in vacuum. R- means the smallest curvature among all the Fe pins, while R+ means the largest.](image)

**Fig. 4.41.** Friction vs. sliding distance for tests of Fe/Cu at 4.07 g, ~22 mm/sec, in vacuum. R- means the smallest curvature among all the Fe pins, while R+ means the largest.

On the effect of surface roughness of the disks, one test was performed for Fe/Cu at 4.07 g load with the Cu disk polished by 400 grit SiC paper only. Typical values of the surface roughness of the disks are given
in Table 4.1. Thus, the Cu disk polished by 400 grit SiC paper is rougher than all other disks in the tests. The friction trace is shown in Fig. 4.42. Compared with a normal Fe/Cu test, the Cu with larger roughness gives lower friction and many spikes. The Fe pin slid on this Cu disk showed large Cu-colored patches.

![Friction vs. Sliding Distance Graph]

Fig. 4.42. Average friction vs. sliding distance for Fe/Cu with different disk roughness. Insert is the friction traces for the two tests.
In summary, the results of sliding friction in each series with 2.88 g load for 10 cycles are as follows:

1. For the Fe/Fe(i) series, friction coefficients of Fe/Fe(Fe) and Fe/Fe are about the same. Friction of Fe/Fe(Cu) varies slightly around the average friction of Fe/Fe.

2. For the Fe(Cu)/Fe(i) and Fe(Fe)/Fe(i) series, friction levels of Fe(Cu)/Fe and Fe(Cu)/Fe(Fe) are about the same, and Fe(Cu)/Fe(Cu) has lower friction compared with Fe(Cu)/Fe. The same trend holds true for the Fe(Fe)/Fe(i) series.

3. For the Cu/Fe(i) series, pure Fe disks give lower friction than the implanted Fe disks. Self implanted Fe(Fe) has slightly higher friction than Fe(Cu) disks.

4. For the Cu(Cu)/Fe(i) and Cu(Fe)/Fe(i) series, the self-implanted Fe(Fe) disks give the lowest friction among the three kinds of disks.

5. For the Fe/Cu(i) series, Cu disks give the highest friction, although there is an exception in tests of each combination. The implanted Cu(Cu) and Cu(Fe) disks behave similarly.

6. For the Cu/Cu(i) series, the self-implanted Cu(Cu) showed lower friction than Cu(Fe), while the values of friction of Cu disks have a large range.

7. Of the single trials, the Fe(Fe)/Cu(i) and Fe(Cu)/Cu(i) series showed that Cu(Fe) disks have the lowest friction, and Cu and Cu(Cu) disks behave similarly. For the Cu(Cu)/Cu(i) and Cu(Fe)/Cu(i) series, the self-implanted Cu(Cu) gives the lowest friction among the three kinds of disks.
4.5.2.A3 Long term tests (> 1200 sliding cycles)

The purpose of the long term tests is to examine the variation of the friction behavior vs. time of sliding and to see if the friction of the ion implanted samples approaches the values for pure samples. Fe pins were used in combinations of Fe/Fe(i) and Fe/Cu(i). Fig. 4.43 shows plots of friction vs. sliding cycles for these tests. For Fe/Fe(i) combinations, a transition from low friction to high friction occurred for most of the tests. Some of the tests on Fe/Fe(Cu) were not long enough for a transition to occur, and they showed very long low friction periods. In the Fe/Cu(i) combination, there is no such transition. Friction traces remained smooth and friction increased slowly. In this case, Hd/Hp <1, which does not fit the hardness ratio criterion (4).
Fig. 4.43. Plots of friction coefficient vs. sliding cycles for long term tests. 
(a) Fe/Fe(i) in early stage. (b) Fe/Fe(i), whole range of sliding distance. (c) Fe/Cu(i). All tests are under 2.88g load, sliding speed is 20–30 mm/sec, in vacuum.
4.5.2.B. Morphology of wear tracks and transfer

With the 36 combinations plus the duplicate tests, there are too many samples of disks and pins or balls to examine all of them by SEM for morphology or by EDS mapping, which is even more costly. Thus, selected groups of samples have been examined for morphology and transfer. Each subgroup will be discussed separately.

1. Cu/Fe(i) combination

The SEM images of the wear scar on the Cu(i) balls and EDS Fe Kα mappings for tests of 0.034 m sliding distance are shown in Fig. 4.44. It is seen that the wear scars are similar and all have grooves on them. The Cu ball in Cu/Fe(Fe) has fewer grooves, and less transfer of Fe to the Cu ball. The transfer of Fe for Cu/Fe(Cu) was larger than for Cu/Fe.
Fig. 4.44 SEM images and EDS Fe mappings of the wear scars on the Cu balls of tests with 2.88 g load, sliding for 0.034 m, in vacuum. (a1, a2) Cu ball in Cu/Fe, (b1, b2) Cu ball in Cu/Fe(Cu), (c1, c2) Cu ball in Cu/Fe(Fe), and (d1, d2) Cu(Fe) ball in Cu(Fe)/Fe.
Fig. 4.44 continued,
Fig. 4.44 continued.
The wear scar morphologies and the amounts of transfer on Cu balls in Cu/Fe(i) sliding for 0.45 m are shown in Fig. 4.45. The EDS analysis is clearer than that for short term Cu balls (as in Fig. 4.44). It is seen that transfer often is associated with deep grooves in the wear scars. The amount of transfer of disk material to Cu balls changes in the order of: Fe(Cu) > Fe or Fe(Fe). The wear scar on the Cu ball in Cu/Fe has rather uniform grooves, and the wear scar on the Cu ball in Cu/Fe(Fe) showed two deep grooves in the center. The wear scar areas of all three Cu balls are about the same.

SEM images of wear tracks on the disks for Cu/Fe(Fe) and Cu/Fe(Cu) are shown in Fig. 4.46. The wear track on the Fe(Fe) disk shows only grooves, while the track on the Fe(Cu) disk shows both grooves and patches which may be caused by transfer (see section 4.4.2).
Fig. 4.45. Wear scars and EDS Fe mappings on the Cu balls for tests at 2.88g load, sliding for 0.45 m, 15–22 mm/sec, in vacuum. (a1), (a2) SEM and EDS on Cu ball in Cu/Fe(Cu), (b1), (b2) on Cu ball in Cu/Fe, (c1), (c2) on Cu ball in Cu/Fe(Fe).
Fig. 4.45 Continued,
Fig. 4.45 continued.
Fig. 4.46. SEM images on wear tracks on disks in (a) Cu/Fe(Fe), (b) Cu/Fe(Cu), under 2.88 g load, ~20 mm/sec, sliding for 0.45 m, in vacuum.
2. Cu(Fe)/Fe(i) combination

The SEM images of the wear scar on the Cu(Fe) ball and the EDS Fe Kα mapping for the test of Cu(Fe)/Fe (<1 cycle) are shown in Fig. 4.47. Transfer occurred mainly at the exit end of the wear scar.

Fig. 4.48 shows the SEM images of the wear scars on Cu(Fe) pins in Cu(Fe)/Fe(Fe) and Cu(Fe)/Fe(Cu) tests under 2.88 g and 10.7 g load, sliding for 0.45 m. The Cu(Fe) balls all have rougher surfaces than that shown in Fig. 4.47. The Cu(Fe) balls in Cu(Fe)/Fe(Cu) showed elongated wear tracks, while Cu(Fe) balls in Cu(Fe)/Fe(Fe) showed nearly round wear areas. This might be due to local curvature variations.
Fig. 4.47. SEM images and EDS Fe Kα mappings of the wear scars on a Cu(Fe) ball of test Cu(Fe)/Fe with 2.88 g load, sliding for 0.034 m, sliding speed ~20 mm/sec, in vacuum.
Fig. 4.48. SEM images on wear areas of Cu(Fe) balls in (a) Cu(Fe)/Fe(Cu), (b) Cu(Fe)/Fe(Fe), both under 10.7 g load, and (c) Cu(Fe)/Fe(Cu), (d) Cu(Fe)/Fe(Fe), both under 2.88g load. Sliding speed was ~20-30 mm/sec, sliding for 0.45 m in vacuum.
Fig. 4.48. Continued.
3. Fe/Fe(i) and Cu/Cu(i) combination

Fig. 4.49 shows the wear morphology of Fe pins in Fe/Fe(i) with 10.7 g load, sliding for 0.45 m. The friction coefficients of Fe/Fe(i) are about the same, but the friction trace for one of the tests of the Fe/Fe combination shows smooth sliding. The same series of tests of the Fe/Fe(Cu) and Fe/Fe(Fe) combinations all show rough sliding with spikes. The wear scar of the Fe pin in Fe/Fe has a small area and porous morphology, while the wear scars of the Fe pins in Fe/Fe(Cu) and Fe/Fe(Fe) contain deep grooves which are associated with rough sliding. SEM images on wear scars of Fe(i) pins for tests under 2.88 g are in agreement with this. In the EDS analysis of the Fe pin for the Fe/Fe(Cu) combination, there is a distinguishable Cu peak, but the amount of Cu was too small to obtain a clear map. In contrast, for Cu/Cu(Fe), as shown in Fig. 4.50, Fe Kα mapping of the wear scar on the Cu ball indicates that transfer was concentrated in the groove and in the patch above another groove.

SEM images of Cu balls for Cu/Cu(i) with 10.7 g load, sliding for 0.45 m are shown in Fig. 4.51. It is seen that the Cu ball in Cu/Cu(Fe) has the most severe wear morphology, and the Cu ball in Cu/Cu has more grooves than Cu/Cu(Cu). As shown previously, the Cu/Cu(Fe) combination gives the highest friction, and Cu/Cu(Cu) has the lowest friction. Thus wear morphology and friction are correlated in this case.

SEM images on the wear tracks on the disks of Cu/Cu(Fe) and Cu/Cu are shown in Fig. 4.52. For Cu/Cu, only different contrast exists on the wear track; for Cu/Cu(Fe), grooves have already formed. However, the two tests have comparable friction.
Fig. 4.49. SEM images of wear areas on Fe(i) pins of (a) Fe/Fe(Cu), (b) Fe/Fe, (c) Fe/Fe(Fe), with 10.7 g load, sliding for 0.45 m, sliding speed ~20 mm/sec, in vacuum.
Fig. 4.49. Continued.
Fig. 4.50 (a) SEM image of the wear scar of Cu ball in Cu/Cu(Fe), under 2.88g, sliding for 0.45 m. (b) Fe Kα mapping of the wear scar in (a).
Fig. 4.51. SEM images of wear scar on Cu balls in (a) Cu/Cu(Fe), (b) Cu/Cu(Cu) and (c) Cu/Cu, with 10.7 g load, sliding for 0.45 m, speed 20~30 mm/sec, in vacuum.
Fig. 4.51. Continued.
Fig. 4.52. SEM images of wear tracks on (a) Cu disk in Cu/Cu and (b) Cu(Fe) disk in Cu/Cu(Fe), under 2.88 g load, ~20 mm/sec, sliding for 0.45 m, in vacuum.
4. Fe(Fe)/Fe(i) combination.

A typical wear scar on Fe(Fe) pins is shown in Fig. 4.53. The contact area is rough and porous.

Fig. 4.53. SEM image of the wear scar on Fe(Fe)/Fe(Cu) at different magnifications, under 2.88 g load, ~20 mm/sec, sliding for 0.45 m in vacuum.
5. Cu(Cu)/all disks.

The surface of Cu(Cu) is different from that of Cu(Fe). There is waviness on the surface, as shown in Fig. 4.54. It is believed that ion implantation contributes to some of the finer roughness on the locally smooth region, such as that labeled A in Fig. 4.54.

Fig. 4.54. A typical wear scar on a Cu(Cu) ball, also showing the surface roughness. In this case, Cu(Cu)/Fe, 2.88 g load, sliding for 0.45 m, ~20 mm/sec, in vacuum.
It has been shown that ion implantation can cause changes in transfer as in the Cu/Fe(Cu) combination and in the wear morphology as in Fe/Fe(Cu). Transfer can cause changes in friction or changes in friction fluctuations as shown in tests with the Fe/Fe(Cu) combination. There is a good correlation in the wear morphology and friction behavior in Fe/Fe(i).
CHAPTER IV
SUMMARY AND CONCLUSIONS

This study was intended to examine the relative contributions of subsurface and surface effects by using ion implantation to modify the sample surface. The original expectation was that differences in sliding behavior between unimplanted samples and self-implanted samples would come from structural changes in the near-surface region due to ion implantation, and differences in sliding behavior between self-implanted samples and samples implanted with different species would come from changes in the surface and near surface chemistry due to ion implantation. However, the experimental conditions were constrained by the shallow depth of the implanted layer. First, contamination from the environment must be reduced as much as possible. Sliding tests have been performed initially using the vertical pin-on-disk geometry with 50 g load. Then a horizontal ball-on-disk setup equipped with a turbo-pump was used to obtain a cleaner environment. Secondly, careful metallographic polishing was required before ion implantation. Despite the efforts in sample preparation, the surface was still rough enough to cause large variations of the nanohardness measurements. Lastly, the proper load for this study had to be identified, because too high a load would mask the effect of ion implantation, while too low a load would make friction subject to the
influence of factors that are negligible with normal test conditions. All of the 36 combinations of tests were completed under low load (2.88 g) with a newly designed loading system. However, at this load level, sliding friction was affected by surface composition, the local surface roughness of the disks, the curvature of the pin samples, the friction in the loading system and signal to noise ratio. Due to these constraints, the goal of studying the relative contributions of the subsurface and surface was not achieved as expected.

Despite the limitations and complications, the following conclusions can be drawn from this study:

1. Comparing the sliding friction behaviors between the pure disks and self-implanted disks with 2.88 g load, the self implanted disks give lower friction than the pure samples for the combinations Cu(Cu)/Fe(Fe), Cu(Fe)/Fe(Fe), Fe/Cu(Cu), Cu(Cu)/Cu(Cu), and Cu(Fe)/Cu(Cu). The decrease in friction ranges from about 0.2 to 0.4 for Fe/Cu(Cu) with respect to Fe/Cu, and about 0.6 for Cu(Fe)/Fe(Fe) with respect to Cu(Fe)/Fe. The self-implanted disks that give friction values similar to those of pure samples are the combinations Fe/Fe(Fe), Fe(Fe)/Fe(Fe), Fe(Cu)/Fe(Fe), Fe(Fe)/Cu(Cu), Fe(Cu)/Cu(Cu), Cu/Cu(Cu). The friction coefficient of the self-implanted disk was increased for Cu/Fe(Fe) compared with Cu/Fe.

The structural modifications by ion implantation have been examined by TEM analysis of back-thinned Fe(i) disks. The original large grains (>100 μm) were refined to 0.02 ~ 0.5 μm by implantation.
The mechanical effect of ion implantation was examined by nanoindentation on the disks. The scatter in the measurements, which resulted from surface roughness, has masked any significant hardening effect due to ion implantation.

2. Comparing the sliding behaviors of self-implanted disks and disks implanted with different species with 2.88 g load, friction trends depend on the ball/disk combination. Those with increasing friction coefficients, compared with the corresponding self-implanted tests, include Fe/Fe(Cu), Cu(Cu)/Fe(Cu), Cu(Fe)/Fe(Cu), Cu/Cu(Fe), Cu(Cu)/Cu(Fe) and Cu(Fe)/Cu(Fe), and the increases range from ~0.01 to 0.3. Those with decreased friction coefficients include Fe(Fe)/Fe(Cu), Fe/Fe(Cu), Fe(Cu)/Fe(Cu), Cu/Fe(Cu) and Fe(Cu)/Cu(Fe). The decreases range from ~0.05 to ~0.35. Friction of Fe/Cu(Fe) does not change significantly compared with that of Fe/Cu(Cu). These changes do not correlate well with adhesion energy changes caused by ion implantation. Local contact events may influence friction in these tests, even though profilometry measurements give similar surface roughness for the two kinds of disks [A(A) and A(B)].

3. The total depth of implanted layers on the disks ranges from 850 to 1200 Å from computer calculation and AES analysis. The maximum concentration of implanted species range from ~4.0 to ~13.0 at. %, with peak depths ranging from 80 to 540 Å. Surface contamination and oxide layers are less than 50 Å thick from AES analysis.

4. Friction transitions were observed in sliding tests on Cu/Fe(i) and Fe/Fe(i) samples at higher loads (30 g and 50 g) and longer sliding distances at 2.88 g load. In most tests, Fe(Cu) disks showed a longer pre-
transition time than Fe(Fe) and Fe disks. After transition, friction levels become similar on all Fe(i) disks, and wear scars on both pins and disks are of typical severe wear morphology with grooves, patches and wear debris.

Long term tests on Fe/Cu(i) at 2.88 g load exhibit a steady increase in friction without a transition.

5. Changes due to ion implantation result in changes in material transfer and wear morphology. For example, the Cu/Fe(Cu) combination has the largest amount of transfer of Fe from Fe(Cu) disks to Cu balls among the Cu/Fe(i) tests at 2.88 g load. The Fe/Fe(Cu) and Fe/Fe(Fe) combinations have the larger wear scars on the Fe pins than Fe/Fe at 2.88 g load.

6. Reduced wear was observed on tests of Cu/Fe(Cu) compared with Cu/Fe at 50 g using a pin-on-disk setup and at 30 g using a ball-on-disk setup. Wear of Fe/Fe(Cu) compared with Fe/Fe was increased under 30 g and 2.88 g loads.

7. A persistence effect was observed with long term tests of Fe/Fe(Cu) at 2.88 g load and Cu/Fe(Cu) at 50 g. This is most likely caused by a geometric effect, in which the implanted material on most of the wear track, especially at the sides, has not worn away.
SUGGESTED FUTURE WORK

The goal of separating the contributions of the surface and subsurface using ion implantation to modify the sample surface in this study was not achieved because of the experimental limitations. More insight into the mechanisms of sliding friction can be obtained using finite element modeling (FEM), which make it possible to examine the effects of parameters such as the applied load, the adhesion energy, the anisotropic plastic deformation and the work-hardening behavior of the sliding components in 3-D simulation. Thus, the limitations of the slip-line field analysis, as in the deformation model of Oxley et al. (15) and in the calculation of Johnson (154), would be removed. The finite element modeling can be conducted with the energy-based model of friction by considering the properties of the metal surface modified by ion implantation and the bulk. The load should be low so that effects of debris particles can be ignored.

The current study exposed several experimental difficulties in studying friction at a few grams load. It serves as a reference for future experimentation. In order to study the mechanisms of sliding friction experimentally, the following conditions must be considered: the investigation should still be conducted in a vacuum chamber to reduce the effect of oxidation and surface contamination. Following this argument,
the chamber should be equipped with a sputtering gun to clean the surface before sliding. Since the time required to form a monolayer of adsorption at room temperature is: 

\[ t = \frac{2.5 \times 10^{-6}}{p(\text{torr})} \text{sec} \] (156), the vacuum pressure should be below \( 10^{-10} \) torr to allow enough time (\( t = 2.8 \) hours) to evacuate the chamber and perform a sliding test. The surface roughening resulting from sputtering can be neglected if a modified AFM can be used under low loads. It should be borne in mind that the level of loads is still critical, because different loads lead to deformation of materials at different depth. The materials chosen can still be pure metals because they simplify the study without complications from second phases and impurities. Characterization of the samples before and after sliding tests should be performed.

The nanohardness measurements in this study were limited by the surface roughness. Further investigations in the nanohardness change due to ion implantation can be conducted by vapor deposition of a film of Cu or Fe on a silica wafer, followed by implantation of the wafer with Fe or Cu. The thickness of the film should be thicker than 10 times of the indentation depth to ensure the measured hardness is representative of the film, and it should be thin enough to ensure smoothness of the film. The porosity in the film and adhesion of the film and the substrate should also be considered.
APPENDIX A

RELATIONSHIP OF MICROHARDNESS AND LOAD FOR Fe & Cu.

Fig. A1. Microhardness vs. load in hardness tests of (a) Fe and (b) Cu.
APPENDIX B
SLIDING WEAR TESTS PROCEDURES ON THE PIN-ON-DISK SETUP

1. Pre-test: check the following:
* the wear track diameter.
* the pendulum itself for sockets, screw direction, strain gauge, and pin position.
* clean the chamber
* the motor speed (18 rpm or 19 for smaller wear track)
* the battery of the strain indicator
* the wire connection: eliminate ground loop by connecting the ground of the strain gauge, the ground of the strain indicator, and the ground (outer shield wires) of the chart recorder and the shielding box.

2. Set up the test (using gloves!):
1). Clean both samples in methanol or ethanol and blow dry (since the test load is low, weight loss would not be detected; thus samples were not weighed).

2). Put the pin in the loading arm (it has to fit in it well when tightening the bolt). Place the loading arm in its frame.

3). Put the disc in the center of the holder, and put the assembly in the bearing housing.

4). Check the position of the loading arm to make sure that the pin touches the disc on the disc centerline.

5). Check to make sure that the loading arm is strictly vertical, using the perpendicular part and the level vial, or align by eye.
6). Remember to tighten the hexagonal key in the motor shaft. Tighten the bolt on the supporting lever.

7). Connect the dead weight to the loading arm; make sure that it goes through the small wheel. It has to be the right load! Connection lines must be appropriate. Too long makes it impossible to load the pin pendulum from outside of the chamber. Tighten the screw on the dead weight.

8). Make sure that the screen covers are over the holes on the base plate.

9). Connect the strain gauge.

10). Make sure the humidity meter is in place.

Switch on the strain gauge indicator and the recorder, check zero level and strain gauge factor of the strain indicator.

11). Lower the bell jar, align the bell jar with the feed-thru collar carefully.

12). Tighten the airlock.

3. Evacuation:

1). Close the main valve to the bell jar and the backing valve.

2). Open the roughing valve and switch on the rotary pump to rough-pump the bell jar.

3). When TC1 is ~300 μm, close the roughing valve and open the backing valve to evacuate the diffusion pump.

4). When TC2 is ~500 μm, open the main valve.

5). When TC1 is ~110 μm, close the main valve, open the water cooling valve, and switch on the diffusion pump heater (Be careful: the vacuum gauge and the diffusion pump heat are controlled by one switch. Never turn on the diffusion pump heater without cooling water on!).

6). When the diffusion pump is warm (~5 minutes), open the main valve to evacuate the bell jar.

7). After ~5 minutes, check the vacuum level by switching on the ionization gauge. When it reaches $2 \times 10^{-5}$ ~ $5 \times 10^{-5}$ Torr, it is ready for wear tests.
4. Wear test:

1). Check revolution counter (turning off the room light will help). Check paper and ink in the pen.

2). When zero line is set on the chart recorder, turn on the motor. Test begins.

3). Keep track of the cycles & speed & observe the samples.

4). When the required # of cycles is over, stop the motor.

5. After the test:

1). Switch off the recorder and strain indicator, and remove the pen.

2). Switch off the diffusion pump heater; close the main valve, leaving the cooling water valve open.

3). Open the air lock and allow air into the bell jar.

4). Raise the bell jar after it has equilibrated with the atmosphere. Remove the specimen by wearing clean gloves. Lower the bell jar.

5). After the diffusion pump has cooled down, close the backing valve and water cooling valve. Switch off the rotary pump. Let air into the rotary pump by opening the roughing valve.
APPENDIX C
SLIDING TEST PROCEDURES ON HORIZONTAL BALL-ON DISK SETUP

A). Setting up the apparatus
1. Clean the samples in methanol or ethanol.
2. Mount the disc by tightening the center screw into the disk supporter.
3. Mount the ball on the loading arm; be sure the holder is vertical.
4. Put the loading arm in place in the chamber, decide the wear track diameter, then tighten the two screws at the pivot point.
5. Align the loading arm: move the balance weight back and forth and choose a point where a higher tilt on the sample end will give a steady position but a lower tilt on the sample end will bring the sample down (approximate balance).
6. Tighten the screw on the balance weight.
7. Put the load on.
8. Connect the lead wires from the strain bridge to the connector on the base of the chamber.
9. Before closing the bell jar, verify that the strain indicator is operating.
10. Close the bell jar, align the bell jar with the feed-thru collar carefully.
11. Tighten the air lock, and open the gate valve, connect the wire between the bell jar and the base plate.
12. Turn on the strip chart recorder so that while pumping is going on, both strain indicator and chart recorder will be warmed up.

B). Pumping
1. Turn on the water cooling for the turbo-pump.
2. Turn on ion-gauge. Beware of the cold cathode gauge as it is at a very high voltage.
3. Check oil in both pumps.
4. Put plugs into the wall, switch on the socket.
5. Turn on the mechanical pump.
6. When TC1 <100, turn on turbo-pump.
7. Keep an eye on the oil level in the reservoir of the turbo-pump during evacuation, injecting oil into the reservoir if necessary.

C). Before & during test
1. Verify if the amplification is at min. or max. mode.
2. Check zero in the indicator, gauge factor = 2.055, set run mode to zero.
3. Verify that adequate paper & ink are available.
4. Turn off the light over the apparatus.
5. When zero line is set on the chart recorder, turn on the motor, test begins.
6. Keep track of the cycles & speed & observe the sample.
7. When the required # of cycles are over, stop the motor.

D). After the test.
1. Shut the gate valve and turn off the turbo-pump. Let prepurified nitrogen into the system gradually (at 10 psi). After 12-15 minutes open the gate valve and verify (by looking thru the bell jar) that the turbo has stopped rotating. Then shut off the mechanical pump. Continue letting the gas into the system until the bell jar comes off the feed-thru collar.
2. Carefully lift the loading arm up, disconnect the lead wires, loosen the screws, and take the beam off, take the ball off and place it in a container, mark the test #, being careful not to mix it with those of other tests.
3. Take the disc off, place it in a container, mark the test #.
4. Clean the system using methanol.
5. Shut off the water supply, switch off the strain indicator and chart recorder, disconnect the plugs from the socket. Lower the bell jar and close the gate valve.
APPENDIX D

DEFINITION OF STANDARD DEVIATION $\sigma$ AND PROBABLE ERROR $E_{\text{prob}}$

Assume $x$ is the variable of interest, and $x_i$ is the measured values of $x$, where $i=1, 2, \ldots, n$. Then, the average of $x$ is:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i,$$

the standard deviation $\sigma$ is:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} |x - x_i|^2}{n - 1}},$$

the probable error is:

$$E_{\text{prob}} = 0.67 \times \sqrt{\frac{\sum_{i=1}^{n} |x - x_i|^2}{n - 1}}.$$

These are two ways of expressing the errors involved in measurements of $x$. As can be seen, the standard deviation is always greater than the probable error.

199
APPENDIX E

A SUMMARY OF THE RESULTS OF 52100 (1/8")/Fe AND 52100/Fe(Cu).

The test parameters are: 50 g, 17 rpm, 2–5 x 10^{-5} Torr; sliding cycles were 100 and 2500. Tests of 52100/Fe and 52100/Fe(Cu) showed very rough sliding. Friction coefficients are summarized in table E.1.

Table E1. Friction coefficients under 50g, 17 rpm and vacuum.

<table>
<thead>
<tr>
<th></th>
<th>initial</th>
<th>jumped to</th>
<th>final</th>
</tr>
</thead>
<tbody>
<tr>
<td>52100/Fe, 100 cycles</td>
<td>0.37</td>
<td>1.22</td>
<td>1.03</td>
</tr>
<tr>
<td>52100/Fe, 2500 cycles</td>
<td>0.36</td>
<td>1.26</td>
<td>0.97</td>
</tr>
<tr>
<td>52100/Fe(Cu), 100</td>
<td>0.32</td>
<td>1.16</td>
<td>1.00</td>
</tr>
<tr>
<td>52100/Fe(Cu), 2500 cycles</td>
<td>0.36</td>
<td>1.13</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Thus friction coefficients were about the same for Fe and Fe(Cu) disks. This probably was caused by the very high contact pressure in this geometry. The wear tracks on the Fe and Fe(Cu) discs are different. Table E.2 shows the profilometer measurements on the disks.
Table E.2 Wear track depth and width(μm) on the discs of tests with 52100 balls, at 50 g load, 17 rpm, in vacuum.

<table>
<thead>
<tr>
<th>sliding cycles</th>
<th>depth (Fe(Cu)/Fe)</th>
<th>width (Fe(Cu)/Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>24.03/31.70</td>
<td>486.25/482.5</td>
</tr>
<tr>
<td>100</td>
<td>5.47/5.22</td>
<td>180.00/245.00</td>
</tr>
</tbody>
</table>

In short term (100 cycle) sliding, the implanted disks showed narrower wear tracks than the Fe disk. In long term (2500 cycle) sliding, the implanted disk showed shallower wear track than the Fe disk. In each condition, the total amount of wear of the implanted disk was less than for the pure disk.

The morphologies of the wear tracks were about the same, consisting of extensive extrusion and deformation, as shown in Fig. E.1. Fig. E.2 shows an example of the wear scar and debris on a 52100 ball.

These tests indicate that under the above test conditions, the implanted disks showed friction behavior and wear morphology similar to those of the pure disks, but the amount of wear was reduced by implantation of Cu in Fe compared with unimplanted Fe disks.
Fig. E.1. SEM image of the wear track on the disks slid with 52100 balls for 2500 cycles. (a) Fe(Cu), (b) Fe.
Fig. E.2. SEM image of (a) the wear scar on a 52100 ball slid on Fe disk for 100 cycles and (b) the debris on the ball.
APPENDIX F

APPROACHES IN SOLVING THE Si PROBLEM

A series of tests was performed with Cu/Fe and Cu/Fe(Cu) after replacing the pins with the balls. A typical track on the disk (Fe(Cu) or Fe) is shown in Fig. F.1. From EDS analysis, it was found that the debris contain a high content of Si. Some Fe disks were examined using SEM/EDS and they did not show Si content. They were then etched so that the subsurface chemistry can be characterized. Only some oxygen was found associated with small oxides (a few μms) in the grain interior. One Cu ball was mechanically polished to remove some material on the surface and the result showed that both the surface and subsurface are of pure Cu. Since Apiezon grease was used throughout this study, the possibility of the chamber being contaminated by the vacuum grease was at first overlooked. Dow-Corning grease which contains silicon may have been used previously. The diffusion pump oil used was unknown. A piece of pure Ag was scratched at the center and Dow-Corning grease and Dow-Corning diffusion oil were applied on each side of the scratch. Both sides showed Si content in AES analysis.

Thus the chamber of the pin-on-disk setup was thoroughly cleaned, and diffusion oil free of Si was used. All the O-rings were changed with some Apiezon vacuum grease (Si free) applied.
Fig. F.1. A typical wear track on an Fe disk with Si contamination from the environment.
APPENDIX G

THE RELATIONSHIP OF FRICTION FORCE MEASURED AND THE THICKNESS OF THE STRAIN GAUGE BACKING BEAM.

The strain gauge backing beam and its stress distribution are illustrated in Fig. G.1.

Fig. G.1. An illustration of the strain gauge backing beam and its stress distribution.
Stress at point \( y \) is:

\[
\sigma = Ky, \quad [G.1]
\]

We also have:

\[
\varepsilon = \frac{\sigma}{E}, \quad [G.2]
\]

\[
\therefore \varepsilon E = Ky, \quad [G.3]
\]

Boundary conditions are:

\[
y = 0, \rightarrow \sigma = 0.
\]

\[
y = \frac{t}{2}, \sigma = \sigma_{\text{max}} = \varepsilon_{\text{max}} E.
\]

\[
\therefore \varepsilon_{\text{max}} E = K \frac{t}{2}, \quad [G.4]
\]

\[
K = \frac{2\varepsilon_{\text{max}} E}{t}, \quad [G.5]
\]

From Momentum conservation:

\[
F_r \cdot l = 2 \int_0^t \sigma(y) \cdot y \cdot dy \cdot b
= 2 \int_0^t Ky^2 b \cdot dy
= 2 \cdot Kb \cdot \frac{y^3}{3} \bigg|_0^t
= \frac{Kbt^3}{12}, \quad [G.6]
\]

From eq. \([G.5]\) and \([G.6]\), we have:

\[
F_r l = 2 \frac{2\varepsilon_{\text{max}} E}{t} \cdot \frac{Kbt^3}{12} = \frac{\varepsilon_{\text{max}} Ebt^2}{6},
\]

Thus:
The maximum strain is related to the voltage output in measuring friction force. For 304 SS, $E = 28 \text{ psi} \times 10^6$. The new strain gauge backing beam has the following dimensions: $b = 22 \text{ mm}$, $t = 1 \text{ mm}$, $l = 10 \sim 11 \text{ mm}$. $F_r = 1 \text{ g}$. 

$$F_r = \frac{e_{max} E b t^2}{6l}. \quad [G.7]$$
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209


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