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UNLUBRICATED FRICTION AND WEAR IN THE Cu-Be SYSTEM

DISSERTATION

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

By
Jarlen Don, B.S.

* * * * *

The Ohio State University

1982

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Chapter I

1 INTRODUCTION

One of the greatest advantages of beryllium copper is its ability to be strengthened by means of low temperature age hardening after the parts have been formed. This characteristic enables the fabricator to produce parts from material that is very formable and to obtain parts with high strength after thermal treatment.

Cu-Be alloys can be precipitation hardened to the highest strength levels attainable in copper-base alloys. They are being frequently used for applications requiring a combination of high electrical conductivity and mechanical strength, and for applications requiring wear and corrosion resistance. For example, beryllium copper has been used for airplane engine crank shaft sleeve bearings, submarine telephone equipment parts, jet aircraft landing gear bearings, etc. Since the late 1960's these materials have almost replaced bronzes and low-alloy steels in problem areas. Properly lubricated beryllium copper surfaces are more wear resistant than those of other copper-base alloys and many ferrous alloys. In fact, in most wear applications, a beryllium copper component is mated with a steel component because there is less chance of galling when a copper-base al-
loy wears against steel. However, unlubricated Cu-Be alloys do not have outstanding wear resistance compared with other copper alloys. As an example (1): an age-hardened beryllium copper wears about two times greater than dispersion hardened copper does.

The major purpose of this study is to investigate the fundamentals of unlubricated sliding friction and wear in Cu-Be alloys. The alloys were heat treated to give a range of hardness values by solution annealing, full age hardening, and overageing. After the wear test detailed structural and chemical information about the block, the debris and the coating of transfer material on the hard sliding ring were carefully examined by using optical microscopy, microhardness tests, scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and fluorescence analysis using energy dispersive techniques (e.g., EDAX) and wave length analysis (WDX). Efforts have been made to make connections between the microstructures and the friction and wear behaviors, and to investigate the effects of precipitates on friction and wear.

The original goal of this project was to try to compare the difference in friction and wear between precipitation hardened copper and dispersion hardened copper (2), e.g., large and stable \( \text{Al}_2\text{O}_3 \) or \( \text{Cu}_2\text{O} \) particles dispersed in cop-
per. It was expected that significant differences would appear which could be related to the possibility of the dissolution (3,4,5) of the particles (precipitates) in Cu-Be and the relative insolubility of the oxide particles in Cu-Al_2O_3 and Cu-Cu_2O. This factor does seem to be responsible for some of the observed sliding behavior.

In addition to the experiments and the microstructural studies, the energy-based friction model (6,7,8) is particularly emphasized in this dissertation. Two theories were developed based on the energy-based friction model, one to predict the thickness of the debris flakes collected from age hardened Cu-Be wear tests and one to explain the shape of the transfer layer on solution annealed wear specimens. The predictions of these theories look promising compared with experiments, and, moreover, they offer some insight into possible wear mechanisms and into formation processes of the transfer layer.

The dissertation is divided into the following eight headings:

(1) Introduction
(2) Literature Survey
(3) Equipment and Experimental Procedure
(4) Experimental Results
(5) Microstructural Evaluations
(6) Theoretical Approaches
(7) Discussion
(8) Summary

The literature survey covers some historical background on Cu-Be alloys and some models for friction and wear. Several new techniques for preparing specimens for microstructural observations are described in Chapter 2. In Chapter 3 and Chapter 4 detailed wear results and structural and chemical information are included, whereas Chapter 5 presents the two theories developed by the author.
Chapter II

2 LITERATURE REVIEW

2.1 Thermodynamic Data of Cu-Be Alloys

In Cu-Be alloys, Pearson (72) reported that there are the following four intermediate phases:

- \( \delta \), "Be\(_2\)Cu", with the ordered fcc structure.
- \( \varepsilon' \), "\( \gamma \)-BeCu", with the ordered bcc(B2) structure.
- \( \beta \), "\( \beta \)-BeCu", with the disordered bcc(A2) structure.

The phase diagram (70,71) of Cu-Be alloys is shown in Fig. (2-1)

2.2 The Precipitation Sequence for Cu-Be Alloys:

The precipitation sequence in Cu-Be alloys has been extensively studied (20-30). There exist a wide variety of interpretations in the literature as to the morphology, crystallography and habit planes of the several intermediate (metastable) phases which form prior to the equilibrium phase. Almost all of the investigators have arrived at a conclusion that:

1. the precipitation processes were initiated with a segregation of Be atoms on \{001\} planes of the matrix, that is, with the formation of plate-like G. P. zones (27,31).
Fig. 2-1 Phase diagram of the Cu-Be system.
(2) the aging sequence is \((\alpha \rightarrow \text{G.P. zone} \rightarrow \gamma'' \rightarrow \gamma' \rightarrow \gamma)\), if the aging temperature is lower than 325°C.

However, there have been dissenting views on the successive processes after the G.P. zone formation. A brief summary on the crystallography and the habit planes of those intermediate phases based on three representative observations \((20, 21, 30)\) is listed in Table \((2-1)\).

2.2.1 Characteristics of Precipitates

Since the morphology and characteristic diffraction patterns of these intermediate phases are important to the microstructural investigations of the wear specimens, the precipitate characteristics found in the literature will be briefly described as follows:

(1) G. P. zones. Most investigators agree that G. P. zones are plate-like monolayers of Be atoms form on the \(\{100\}\) planes of the Cu-rich matrix during early aging stages. They cause characteristic continuous \(<100>\) streaks on the electron diffraction pattern. Dark field electron microscopy \((21)\) performed at a position along one of the \(<100>\) streaks shows that the size of the plate is about 100Å in diameter and 10Å thick.

(2) \(\gamma''\) phase. Further aging of the solution annealed specimen results in the "bunching up" of the \(<100>\) streaks near the \(2/3 \{200\}\) reciprocal lattice positions. An increase in intensity near the \(1/3 \{200\}\) positions
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<tr>
<td>Rioja (20)</td>
<td>a=b=2.7 Å, c=2.56 Å</td>
<td>bct, bcc, B2</td>
<td>(110) // (100), (112) // (120)</td>
</tr>
<tr>
<td>Geisler</td>
<td>a=b=2.54 Å, c=3.24 Å</td>
<td>bc monoclinic</td>
<td>(111) // (111), (112) // (120), (110) // (110)</td>
</tr>
<tr>
<td>Shimizu</td>
<td>a=b=2.53 Å, c=2.9 Å</td>
<td>bct, bcc, B2</td>
<td>(001) // (001), (110) // (130), (113) // (103), (110) // (110), (110) // (010)</td>
</tr>
</tbody>
</table>
is also observed, but this is usually attributed to double diffraction from the \{200\} reflections (20). The phase also has a habit plane (100) and the plates line up along the traces of the \{110\} planes on \{100\} foils. The X-ray diffraction results led Geisler et al. (30), to proposed that the crystal structure of \(\gamma''\) was body centered monoclinic with \(\beta = 85^\circ 25'\) and \(c/a = 3.24\AA : 2.54\AA\). However, Shimizu attributed the 2/3(200) reflection (\(d = 2.9\AA\)) to the piling up of G. P. zones on every other (100) plane and claimed the \(\gamma''\) has a body centered tetragonal structure with: \(a_{\gamma''} = \frac{a_{\gamma}}{\sqrt{2}} = 2.53\AA\) and \(c_{\gamma''} = 2.9\AA\)

3) \(\gamma'\) phase. With further aging the 2/3\{200\} reflections fan out into an "arrowhead"-like shape. Geisler (30) reported that the \(\gamma'\) phase has \(a = 2.79\AA\) and \(c = 2.54\AA\) with the following crystallographic orientation with respect to the matrix:
\[
\begin{align*}
(\overline{1}12)_{\gamma} & \parallel (\overline{1}20)_{\gamma'} \\
(\overline{1}10)_{\gamma} & \parallel (001)_{\gamma'}
\end{align*}
\]
Shimuzu (20) proposed that \(\gamma'\) is a cubic phase with \(a = 2.7\AA\) and the following orientation relationship:
\[
\begin{align*}
(\overline{1}13)_{\gamma} & \parallel (130)_{\gamma'} \\
(110)_{\gamma} & \parallel (001)_{\gamma'}
\end{align*}
\]
However, Rioja (21) claimed that the "arrowhead" reflections continuously change into more or less discrete reflections which are elongated along the <113>
directions, without any crystal structure change. Therefore, he concluded that the \( \psi \) phase at the early stages has the (112) habit plane, but the (112) habit plane changes to the \( \{113\} \) planes accompanied by c-axis expansion toward 2.7\( \AA \) as the precipitates continue to grow.

(4) \( \gamma \) phase. The equilibrium \( \gamma \) phase has the B2 structure and the lattice parameter \( a = 2.7\AA \). Rioja reported that two crystallographic orientation relationships were found. When the phase formed after \( \psi \) phase, the Bain orientation was observed. That is

\[
\begin{align*}
(110)_\alpha & \parallel (100)_\gamma \\
(100)_\alpha & \parallel (100)_\gamma
\end{align*}
\]

But when the phase forms directly from the supersaturated \( \alpha \) matrix, the Kurdjumov-Sachs (32) orientation was observed, i.e.,

\[
\begin{align*}
(111)_\alpha & \parallel (101)_\gamma \\
(\bar{1}1\bar{0})_\alpha & \parallel (111)_\gamma
\end{align*}
\]

2.2.2 Precipitation Sequence:

Rioja reported that the precipitation sequence below 325°C is \( \Gamma \rightarrow \psi \rightarrow \psi \rightarrow \Gamma \), while above 325°C, it is \( \Gamma \rightarrow \psi \rightarrow \gamma \). Similar reports by Gruhl (33) and Wilkes (24) also indicated the differentiation in precipitation sequence between aging above and below 325°C. In addition to those four phases, Rioja claimed that an equiaxed zone con-
sisting of clusters of Be enriched regions, approximately 15-30Å in diameter, was observed prior to the plate-like G.P. zones. This was attributed to Lee, Barnett and Aaronson (34) which suggested that if "fcc Be zones" are elastically harder than an fcc Cu matrix, the zones should have a spherical shape to minimize strain energy. Also the spherical zones minimize the surface energy if the surface energy is assumed to be isotropic. The reason for the equiaxed zones G.P. zones transformation is simply because the 12% lattice mismatch prohibits the growth of these clusters beyond 50Å.

2.2.3 Effect of Alloying Elements on Precipitation

Cobalt was added to the commercial Cu-Be alloys mainly for two reasons: (1) to aid grain refinement (2) to reduce the precipitation rate. Bonfield (35) reported that cobalt retards the discontinuous reaction below 380°C by modifying the grain-boundary structure and affecting the grain boundary step density and, hence, the boundary mobility. Henmi (36) also demonstrated that the grain boundary motion is slowed by the presence of cobalt due to the low diffusivity of Co in the Cu-Be 25 alloy. To explain the suppression of the precipitation rate, Henmi (36) and Wynn (25) suggested that the vacancy-Co pair is hardly mobile in Cu-Be alloys and hence the 'γ' is retarded due to the lack of mobile vacancies. A similar reason was given by Murakami et al (26) to explain that Co suppresses G.P.-zone formation. Murakami et al also concluded that Mg and Zn accelerate clustering and
the G. P. zone formation, while the elements Co and iron suppress them. On the other hand, Mg and Fe accelerate the precipitation because they reduce the coherency strains.

2.3 Mechanical Properties of Cu-Be Alloys

It could be argued that almost every mechanical property of a metal has an effect on its friction and wear behavior, either directly or indirectly as a result of effects on surface contacts, subsurface deformation and fracture. Although such influences are controversial and have been considerably debated over the years, it is still worthwhile to document the relevant mechanical properties of the Cu-Be alloys for possible correlation with wear studies.

Table 2-2 (37) is a list of the mechanical properties of the commercial full-hardened 25 alloy. In addition to the fully hardened alloy, the mechanical properties of alloys with different heat treatments are also of interest to this investigation. As an example of the effect of aging temperature on the hardness changes, the reports from Murakami et al (26) and Wynn (25) are shown in Fig. 2-2. When aged at 80°C, the hardening was very slow. The aging curve at 135°C shows the one-stage hardening due to the G. P. zone formation. Further, when aged at 200° and 250°C, the specimen hardens by the two-stage hardening corresponding to the zone formation and precipitation of the intermediate phase. In the isothermal aging curve at 350°C, a rapid and large
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat treatment</td>
<td>315°C 3 hours</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>165–195,000 psi (1140–1340 Mpa)</td>
</tr>
<tr>
<td>Yield strength</td>
<td>140–175,000 psi (970–1210 Mpa)</td>
</tr>
<tr>
<td>Elongation</td>
<td>4–10% in 2 in.</td>
</tr>
<tr>
<td>Fatigue strength (10 cycle)</td>
<td>35–38,000 psi</td>
</tr>
<tr>
<td>Hardness</td>
<td>Rc 36–41</td>
</tr>
<tr>
<td></td>
<td>DPH 353–382</td>
</tr>
</tbody>
</table>
HARDNESS VS. AGING

Fig. 2-2 The influences of aging temperature and aging time on micro-Vickers hardness.

- \( \times \) : aging at 135°C (26)
- \( \square \) : aging at 200°C (26)
- \( \circ \) : aging at 250°C (26)
- \( \triangle \) : aging at 350°C (26)
- \( \mathcal{X} \) : aging at 325°C (25)
increase in strength due to $\gamma'$ precipitation is followed by an overaging and softening. Fig. (2-3) (36) shows the hardness of Cu-2% Be and Cu-Be 25 alloys aged at 2 hours at various temperatures between 120°C and 350°C. The Cu-2% Be alloy hardens at 250°C and attains a maximum at 275°C, while Cu-Be 25 alloy hardens at 275°C and the hardness attains a maximum at 315°C. The aging temperature range which attained the maximum hardness in the Cu-Be 25 alloy is wider than that in a Cu-2% Be alloy. The effect of aging on the mechanical properties (37) other than hardness, such as ultimate tensile strength, yield strength, and elongation, is shown in Fig. 2-4a, Fig. 2-4b and Fig. 2-4c.

The characteristic stress-strain curves for precipitate sizes from 80 to 350Å reported by Gadalla (38) is shown in Fig. (2-5). All curves show a quasiparabolic work-hardening when the strain is below about 70%. Negligible serrations were found by Gadalla immediately following yielding.

However, it should be pointed out that transfer material often exists at the interface of a sliding pair. It has been widely acknowledged that transfer material plays a significant role in friction and wear behavior (16, 40, 39) Since the transfer material can have entirely different structure, chemistry and properties from the original test material, it is inappropriate to explain friction and wear only by knowledge of the material to be tested. Unfortunately, very
Fig. 2-3 Changes in hardness of Cu-2%Be and Cu-Be 25 alloy aged at 2 hours at various temperatures (36).

X : Cu-2%Be
O : Cu-Be 25 alloy
Fig. 2-4 Effect of aging on mechanical properties. (a) ultimate tensile strength (t) yield strength (c) elongation.

SOLUTION ANNEALED
BRUSH ALLOY 25

- Ultimate Tensile Strength vs. Temperature
- Yield Tensile Strength vs. Temperature
- Elongation vs. Temperature
Fig. 2-5 Stress-strain curves for Cu-Fe alloy with different heat treatment.
little information about transfer material can be found in the literature, partly because of experimental difficulties in obtaining reliable data.

2.4 Plastic Deformation of Cu-Be Alloy

Although there is extensive literature on Cu-Be alloys, especially in connection with precipitation, there appears to be little information concerning the plastic deformation of these alloys. In his microstructural studies of plastically deformed polycrystalline Cu-Be alloys, Gadalla (38) reported that deformation twins were observed in age hardened specimens due to the low stacking fault energy in the Cu-Be system (41). The parabolic stress-strain curve at low strains was interpreted by using Orowan's theory for parabolic work-hardening due to undeformable particles. Henmi reported that deformation twins and dislocation structure are observed after plastic deformation of specimens aged 2 hours at 120°C. The dislocations did not form a cell structure; instead, they formed a structure similar to those observed in Ag (41), Cu-Zn (42) and Cu-Sn (43), all of which are low stacking fault energy materials.

Kelly (29) performed some experiments on the plastic deformation of age hardened single crystals of Cu-Be alloys. Easy glide and well defined primary slip lines appeared on under-aged specimens, and the orientation changes during extension were quite consistent with those in specimens de-
formed by single slip. The tensile axes overshot the \(<001>-<111>\) boundary by up to 7°. On the other hand, no easy glide was found in an overaged specimen, and the specimen showed a small amount of rotation. Three distinct sets of slip lines could be detected on the crystal, therefore the authors concluded that the overaged crystal was deformed by multiple slip.
2.5 Review of Data Regarding Friction and Wear in Cu-Be Alloys

Precipitation hardened Cu-Be alloys have excellent high load bearing properties at temperatures to 250°C when used with the proper lubricant and against hardened steel. They have been used to replace bronzes and low-alloy steels in many areas for meeting increased stress and bearing requirements. However, their friction and wear performance tends to be affected by factors such as hardness, vacuum, alloying elements and moisture. Some previous work concerning these factors will be reviewed in the following section.

2.5.1 Effect of Hardness

It is common knowledge that the friction of hard substances, such as tungsten carbide, hard chromium, hard steel, etc., is somewhat less than that of softer metals. Buckley (54) reported that the friction coefficient decreased as hardness increased for several crystallographic orientations on tungsten as well as other inorganic crystals. Similar reports of the hardness effect on friction in Cu-Sn (55), Cu-Al (56), and polymers (57) also indicated that friction often decreases as hardness increases. The friction of heat-treated Cu-Be alloys also decreases with increasing hardness.

Moore and Tegart (58) conducted a friction test using a hard steel slider and a long Cu-2% Be plate, which had been
heat-treated to give a range of hardness along its length. The specimen was heat treated such that the upper end was overaged, the lower end was underaged and the center region was fully hardened. The result showed a minimum friction of 0.4 at the center, which is fully hardened, and higher friction coefficients (about 0.9) near both ends, where it is soft. Furthermore, they claimed that there was considerable pick-up of material from the plate to the steel slider, and when a diamond slider was used the pick-up was considerably reduced. The slope of the linear friction vs. hardness plot for the diamond slider was less than for the steel slider, i.e., the effect of hardness on friction was stronger for the steel slider than for the diamond slider.

A similar hardness effect in Cu-Be 25 alloy was reported by Jellison et al (59). They performed unlubricated tests in air as well as in vacuum with heat treated Cu-Be 25 alloys sliding against steel. The friction coefficient was found to decrease as the specimen hardness increased in both vacuum and air.

2.5.2 Effect of Lubricant and Moisture

The friction and wear performances of Cu-Be alloys are excellent when used with proper lubricants (60,61,62). Furthermore, the presence of moisture in lubricants, even in small amounts such as would be picked up from exposure to humid atmospheres, has a significant effect on the wear be-
behavior. An example of the effects of lubricant and moisture is shown in Fig. (2-6) (Courtesy of Wikle). Paine (62) pointed out that the presence of moisture in a lubricant reduced wear rate by several orders of magnitude. This effect appeared to be independent of the type of lubricant.

2.5.3 Effect Of Vacuum

Numerous studies have been focused on the effect of vacuum on friction and wear. For example, Buckley (54) has measured friction coefficients for a variety of metals in high vacuum and correlated these results with crystal structure, orientation and applied load. Evans and Monroe (63) reviewed the phenomenon of surface welding in high vacuum. These studies indicated that some friction coefficients for pure metals sliding on themselves could be as high as 6.5 in high vacuum.

With Cu-Be 25 alloys sliding against steel, Jellinson reported that the friction coefficients of solution annealed Cu-Be and solution annealed plus 1/4 work hardened Cu-Be increased as the pressure decreased from 760 torr to $10^{-8}$ torr, while, on the contrary, for fully age hardened Cu-Be the friction coefficient decreased slightly when the degree of vacuum increased from 760 torr to $10^{-8}$ torr. The friction trace for the fully age hardened Cu-Be was also quite different from that for the solution annealed + 1/4 work hardened Cu-Be, as shown in Fig. (2-7)
Fig. 2-6 Results of wear test show effect of moisture on wear depth. A highly refined white mineral oil was used in test. (courtesy of K. Wikle)

Fig. 2-7 Friction traces for Cu-Be alloys under different vacuum conditions. (courtesy of Jellison (59))
ANN & 1/4 H: solution annealing followed by 25% work hardening.
1/4 HT: aging at 320°C for 2 hours.
(courtesy of Jellison et al). The maximum coefficient of friction for solution annealed plus 1/4 work hardened specimen was nearly the same in air and in vacuum, but the coefficients at the end of the test were different. In air the maximum of 1.33 was reached early in the test and decreased and leveled off thereafter. At $10^{-8}$ torr, however, the maximum occurred much later and remained constant thereafter. The friction trace for age-hardened Cu-Be rose to a maximum of about 0.9 and then remained nearly constant at a value very similar to the annealed specimen tested in air.

2.5.4 Effect of Alloying Elements

Wear resistance can be further enhanced by incorporating a dispersion of a hard phase of cobalt beryllide (CoBe). In Wikle's report, he demonstrated that wear resistance could be significantly enhanced by increasing both the contents of Co and Be. For example, Cu-2.5Be-2.5Co alloys wear several orders of magnitude more slowly than either Cu-1.9Be-2.5Co alloys.

Ni has been reported (64) to have an effect, similar to that of Co. The addition of Ni accompanied by increasing Be content gives much improved wear resistance due to the presence of NiBe particles. When a proper lubricant was used, addition of Pb to Cu-Be 25 alloy has a beneficial effect on wear performance (64). About 0.25% Pb seems to contribute a maximum effect on lubricated wear resistance.
In addition to alloying elements, some surface treatments such as shot peening, surface pre-oxidation, placing graphite on the surface, ... etc. will also improve the wear resistance. Tucker and Traub (119) indicated that wear properties can be increased by orders of magnitude by plasma depositing atomized Cu-Be powders on the surface. There was a thin BeO film on the surface of each spherical particle before plasma deposition. Thus, after deposition a network of BeO films exist throughout the coating structure. It is interesting to point out that the optical micrograph (65) of the plasma coated layer has a layered flowing feature, which looks very similar to the transfer layer (66) near a wear surface.

2.5.5 Friction and Wear in Other Precipitation Hardened Alloys

(1) In Al-4 wt% Cu Alloys

The maximum hardness of precipitation hardened Al-Cu alloys aged at 165°C is about 100 kg/mm² (68,67), while that of the solution annealed and over-aged Al-Cu is 60 kg/mm² and 70 kg/mm², respectively. Wilman (67) reported that the minimum friction coefficient during abrasion occurred exactly when the alloy was fully age hardened. This effect was attributed to the maximum hardness. However, comparing the effect of precipitation hardening to that of the work hardening, Wilman claimed that precipitation hardening appeared
to have much greater influence on friction. The wear resistance of this alloy behaves similarly to the friction coefficient, i.e., fully age hardened Al-Cu wears less than either solution annealed or over aged Al-Cu.

(2) In Cu-Cr Alloys

In contrast to Wilman's work, Suh (69) reported that the friction coefficient of Cu-Cr alloys was almost unaffected by precipitation hardening during dry sliding, although the fully age hardened alloy (140 kg/mm²) was about 70 kg/mm² harder than the over-aged alloy. Suh claimed that the wear resistance was affected by aging, but the maximum wear resistance occurred at aging times shorter than those which yield maximum hardness. The explanation Suh proposed was that crack nucleation occurs easily near the maximum hardness.
2.6 Adhesion Theory

The most widely accepted theory of friction today is an adhesion theory proposed by Bowden and Tabor (16, 44, 45, 46). It incorporates adhesion of surface asperities to form junctions, growth of the junction area and shear at or near the junctions. Two main contributions to sliding friction have been proposed by Bowden and Tabor, i.e., an adhesion term and a plowing term. However, it seems that they have mainly concentrated on the deformation and shearing of asperities and on the junctions which these may form.

When two surfaces are placed together and slide against each other, they make contact over the tips of their asperities and the pressure on the contacts can be extremely high. Over these regions where intimate contact occurs, strong adhesion takes place and the separate specimens become, in effect, a continuous solid. The force needed to shear these junctions is therefore responsible for the "shearing term" in Bowden and Tabor's model. If one surface is much harder than the other, the asperities on the harder surface will plow out grooves in the softer one and this will contribute an additional "plowing term."

Based on the assumption of two contributions to friction, the total frictional force may be written as

\[ F = S + P \]

where \( S \) = the force required to shear the
metallic junctions
and \( P = \) the force required to displace the softer metal from the front of the rider.

If \( \tau_{\text{jct}} \) is the shear strength of the adhesive junctions, then the shearing term \( S \), is equal to \( A \cdot \tau_{\text{jct}} \), where \( A \) is the total contact area. Since the normal load \( L \) is supported by the total contact area \( A \) of the elastically and plastically deformed asperities, \( S \) may be written as

\[
S = A \cdot \tau_{\text{jct}}
\]

\[
= \frac{L}{P_o} \tau_{\text{jct}} \tag{2-2}
\]

where \( P_o \) is the yield pressure of the specimen.

Bowden and Tabor performed some experiments (16,64) which showed that \( \tau_{\text{jct}} \) is roughly equal to the bulk shear strength of the softer metal of the sliding pair. Therefore, to a first approximation, \( S \) of a clean metal is determined by their strength properties \( \tau \) and \( P_o \).

The plowing term, \( P \), may be calculated for different shapes of asperities by setting the friction force equal to the force needed to displace material during the formation of grooves. For example, for a hemispherical rider as shown in Fig. (2-8)

\[ \text{Fig. 2-8 Sketch showing the plowing effect} \]
\[ P = A' \times P' \]

where \( A' \) = the contact area

\[ P' = \text{the pressure needed to displace the material} \]

and \( P' \) may be expected to be of the same order as \( P_0 \) and \( A' \) is approximately equal to \( 1/12 \, d^3/r \). Therefore, combining Eq. (2-2) and Eq. (2-3) gives the result for the friction force of a hard hemispherical rider sliding against a soft material

\[ F = \frac{L}{P_0} \tau + \frac{1}{12} \frac{d^3}{Y} \]

Including both contributions to the friction coefficient, \( \mu = \mu_a + \mu_p \), Bowden and Tabor concluded that for smooth sliding \( \mu_a \) would dominate and for abrasion \( \mu_p \) would be more important.

The adhesion theory can be extended to include surface films which reduce the junction shear strength to \( \tau_i \). Bowden and Tabor demonstrated that the friction coefficient is then \( \mu \sim (-1 + 1/K^2)^{-1} \), where \( K = \tau_i / \tau_{\text{max}} \). Thus, for small \( K \), \( \mu \) can be very small, but for \( K \) approaching one, \( \mu \) grows rapidly. The model does not work well for \( K = 1 \) (a metal coated with itself) or for \( K > 1 \) (a hard coating).

Based on an idea similar to Bowden's and Tabor's adhesion theory, Halling (17) included both the junction shear
strength, \( \tau \), and the yield pressure, \( P_0 \) (analogous to penetration hardness), to treat the friction coefficient of coated systems. He was able to predict a maximum for a hard coating and a minimum for a soft coating, as observed experimentally.

The principal results of the adhesion theory are reasonable and are widely accepted; however, several investigators have raised fundamental questions about the theory (47, 48), while some others have offered alternatives to adhesion theory (49). Basically, the adhesion theory does not account for either the severe subsurface plastic deformation or the transfer material which develops on both surfaces of the sliding pair.
2.7 Delamination Theory of Wear

Suh (50-54) has introduced delamination theories of wear. In his original theory (1973), a soft surface layer due to dislocation image forces near the wear surface was emphasized. Suh assumed that below the soft layer was a region with higher dislocation densities due to the vanishing of the image force. Therefore, nucleation of voids may take place at a certain distance below the surface as a result of dislocation pile-ups. Nucleation of voids will be enhanced if the material contains hard second phase particles for dislocations to pile against. Subsequent voids coalesce, either by growth or shearing of the material, which will result in cracks parallel to the surface and eventually to flake-like debris.

One problem with this model is that the assumed soft surface layer would only be a few hundred Å thick, whereas the wear particles can be much thicker (tens of μm). Since 1973 Suh has omitted reference to the soft surface layer and presented a number of alternative analyses to explain subsurface void formation and crack propagation based on plastic deformation, stress analysis and fracture mechanics. In an overview paper (51) of his delamination ideas, Suh presented the basic sequence of events for wear particle formation as:
(1) Asperity deformation (soft body) and smoothing of the wear surface. Each point along the softer surface experiences cyclic loading as the asperities of the harder surface plow it.

(2) The surface deformation exerted by the harder asperities on the softer surface includes plastic shear deformation which accumulates with repeated loading.

(3) As the subsurface deformation continues, cracks are nucleated below the surface. Crack nucleation very near the surface is not favored because of the highly compressive stress existing below there.

(4) Once cracks are present, further loading and deformation causes cracks to extend and to propagate due to a maximum tensile stress below the surface.

(5) When these cracks finally shear to the surface long and thin wear sheets delaminate.
2-8 Energy Based Friction Model

Friction is often regarded as purely a surface process, as in the adhesion theory. However, it usually involves changes in the structure and properties below the surfaces of the sliding pair and heat dissipated as a result of the work done by frictional force. The heat dissipated during sliding is very closely related to the subsurface plastic deformation (9,10). As a matter of fact, Hirth and Rigney (11) pointed out that the principal mechanism for the dissipation of friction work is through plastic deformation.

Since plastic deformation can be expressed by familiar parameters such as stress and strain, the energy required to cause such plastic deformation can be easily calculated from the stress-strain curves (note that only a small fraction of this energy will be stored in the system; instead, most of the energy transforms into heat and is dissipated (9). Therefore, the relation between the frictional force and the subsurface plastic deformation can be obtained by balancing the work done by the frictional force and the subsurface plastic energy with the ease of plastic deformation and associated parameters. It should be pointed out that the energy is indeed balanced by doing so because:

\[
\text{work done by frictional force (energy input)} = \text{heat dissipated} + \text{elastic energy stored in the system (energy output)}
\]
= energy calculated by the area under stress-strain curve.
That is to say, the heat dissipated has already been considered by the energy under the stress-strain curve.

Since the subsurface strain is usually extremely high, the elastic energy term may be ignored. As a result, the main assumption of the Energy-based friction model may be stated as:
The friction work done is equal to the work of plastic deformation.

2.8.1 Early Friction Calculations

In reference (12) Rigney described a very simple energy-based model in which sliding of a hard slider on a softer sample material caused a well-defined highly-deformed layer to form near the surface of the sample. If the material in this layer had well-defined properties and a well-defined thickness t, one could calculate a simple expression for the friction coefficient, as below

\[ W_P = \mu \cdot L \cdot \delta x_s \] 2-6

\[ W_{F} = \int \tau \cdot \varepsilon \cdot dV \] 2-7

where \( W_F \) = work done by frictional force
\( W_{P} \) = plastic energy
\( \mu \) = friction coefficient
\( L \) = normal load
\( t = \) thickness of the highly deformed layer (HDL)

\( \tau = \) shear strength of the HDL

\( \varepsilon = \) shear strain in HDL

\( \delta x_5 = \) small increment of distance the slider advances

Therefore,

\[
\mu = \frac{\omega t \tau \varepsilon}{L} \tag{2-8}
\]

This simple model can readily be applied to self-mated tests and to coatings because energy terms are additive, and therefore each deformed region contributes a term to the friction.

2.8.2 Improved Friction Model

It is well known that displacements fall off rapidly and smoothly below sliding interfaces (13, 14, 19). Longitudinal sections of worn samples show that the displacement profile may be described by a simple exponential decay, \( \exp(-az) \), where \( z \) is the depth below the interface and "a" is a decay constant which describes the depth of the deformation.

Because the stress and the strain depend strongly on the depth below the interface, i.e., the stress, strain and the deformation zone are not so well-defined as was expected in the early friction model of section (2.8.1), Heilmann and Rigney (7, 8) modified the friction model by using a more realistic stress-strain curve and an exponential-decaying displacement field. The stress-strain relation used was
\[ \tau = \tau_{\text{max}} \left( 1 - \exp (-c\gamma) \right)^{\frac{1}{2}}. \quad 2-9 \]

(c is a constant related to work hardening rate) which saturates at \( \gamma_{\text{max}} \), a material property, and reduces to a simple power law at low strains, i.e., \( \gamma \sim \gamma^{\frac{1}{2}} \). Eq. (2-9) is similar to the \( \gamma - \gamma \) relation introduced by Voce (15). The displacement field used by Heilmann and Rigney was described by a simple exponential function, as

\[ \delta x(z) = \delta x_s \, e^{-az}. \quad 2-10 \]

where

- \( \delta x(z) \) = displacement at depth \( z \)
- \( \delta x_s \) = displacement at surface
- \( a \) = decay constant
- \( z \) = depth below the interface

Once the stress-strain relation and the displacement field are determined, the friction calculation can be derived based on the same approach used in the earlier model, i.e., friction work is equal to plastic work, or

\[ W_p = \int \tau(Y) \Delta \gamma dV = W_{\text{p}}. \quad 2-11 \]

The volume integral can be converted to an integral over the depth \( z \) by using \( dV = NAdz \), where \( N \) is the number of contacting asperities and \( A \) is the average area of an asperity. In order to integrate Eq. (2-11), the relation between \( \gamma(\gamma), \Delta \gamma(z) \) and \( z \) has to be determined. From Eq. (2-10) \( \Delta \gamma(z) \) can be obtained as

\[ \Delta \gamma(z) = - \frac{\partial}{\partial z} \delta x(z) = a \delta x_s \, e^{-az}. \quad 2-12 \]

and \( \gamma(z) \) may be written as

\[ \gamma(z) = \gamma_s \, e^{-az}. \quad 2-13 \]
Therefore, the average surface strain can be found from Eq. (2-9) and Eq. (2-13) in terms of the stress $\tau_s$ and $\tau_{\text{max}}$:

$$\gamma_s = -\frac{1}{c} \ln(1- (\tau_s/\tau_{\text{max}})^2)$$  \hspace{1cm} 2-14

Combining Eq. (2-9), Eq. (2-13) and Eq. (2-14) yields an expression for $\tau(z)$:

$$\tau(z) = \tau_{\text{max}} \left(1 - [1 - (\tau_s/\tau_{\text{max}})^2] e^{-az}\right)^{\frac{1}{2}}.$$  \hspace{1cm} 2-15

Up to this point, the expression for the plastic work may be obtained by combining Eq. (2-11), Eq. (2-12) and Eq. (2-15):

$$W_p = N \cdot A \cdot \tau_{\text{max}} \cdot a \cdot \varepsilon_s \cdot \int_0^\infty \left(1 - [1 - (\tau_s/\tau_{\text{max}})^2] e^{-az}\right)^{\frac{1}{2}} e^{-az} \, dz.$$  \hspace{1cm} 2-16

The solution to this equation is

$$W_p = N \cdot A \cdot \varepsilon_s \cdot \tau_{\text{max}} \cdot F\left(\frac{\tau_s}{\tau_{\text{max}}}\right),$$  \hspace{1cm} 2-17

with $F(U) = 1 - 2\left(\frac{\ln(1+u) - u}{\ln(1-u^2)}\right)$. The function $F(U)$ rises smoothly from zero to one as $U$ rises from zero to one, as shown in Fig. (2-9).

The friction coefficient can now be obtained by Eq. (2-17) and Eq. (2-6)

$$\mu = \frac{NA}{L} \tau_{\text{max}} \cdot F\left(\frac{\tau_s}{\tau_{\text{max}}}\right).$$  \hspace{1cm} 2-18
Fig. 2-9 Dependence of the function $F(u)$ on $u = \frac{\tau_s}{\tau_{m,x}}$. $F(u) \rightarrow 1$ as $\tau_s \rightarrow \tau_{m,x}$. 

\[ F(u) = 1 - 2 \left( \frac{\ln(1+u) - u}{\ln(1-u^2)} \right) \]
At steady state $\tau_s$ is equal to $\tau_{\text{max}}$, therefore the steady state friction coefficient is equal to $\frac{NA}{L} \tau_{\text{max}}$. The result is very similar to that of the well-known adhesion theory (16).

2.8.3 Application to Coated Systems

The energy-based friction model can be extended to treat coated systems, e.g., transfer layer on substrate. Because the terms for work dissipated in different deforming materials are additive and each gives a contribution to the friction coefficient.

The work done in a coating of thickness $T$ can be obtained by integrating Eq. (2-16) from 0 to $T$ and inserting parameters for the coating material. Therefore, the result is

$$W_{pl}^L = NA^L \xi_s L \tau_{\text{max}}^L \left[ F(\tau_s^L / \tau_{\text{max}}^L) - e^{-a^L / T} F(\tau_I^L / \tau_{\text{max}}^L) \right]$$

where terms with superscripts $L$ represent the parameters for the coating material, and $\tau_s^L$ represents the average shear stress at the coating/base interface.

The deformation in the base material also has to be considered. Assuming the stress and the displacement to be continuous at the interface, one can derive the energy term for the base material without difficulties. The result of combining both contributions for the coated system is thus

$$\mu(T) = \frac{NA^L}{L} \left[ \tau_{\text{max}}^L \left( F(\tau_s^L / \tau_{\text{max}}^L) - e^{-a^L / T} F(\tau_I^L / \tau_{\text{max}}^L) \right) \right]$$
Eq. (2-20) does not give reasonable results when the coating is very thin because the contact area is then determined by the base material. Therefore, Heilmann and Rigney imposed a correction function, which is

\[ f(T) = \frac{1}{2} \left( \tanh(U - VT) + 1 \right) \]

for thin coatings. \( f(T) \) is the fraction of asperities which is uncoated for a given average coating thickness \( T \); the fraction of coated asperities is then \( 1 - f(T) \). The function \( f(T) \) is adjusted so that the point of inflection is at \( T = U/V \). The friction expression after correction is then

\[
u(T) = (1 - f(T)) \frac{N A^L}{L} \left[ \tau_{max} \left( F\left(\frac{\tau_s}{\tau_{max}}\right) - e^{-a^L T} F\left(\frac{\tau_I}{\tau_{max}}\right)\right) + \tau_{max} e^{-a^L T} F\left(\frac{\tau_I}{\tau_{max}}\right)\right] + f(T) \frac{N A}{L} \tau_{max} F\left(\frac{\tau_s}{\tau_{max}}\right).
\]

Eq. (2-22) is able to predict a maximum when a hard material is coated on soft base and a minimum when soft coating is on hard base. These predictions were in good agreement with experiments reported by Halling (17) and Suh (18).
2.9 Relation Between Wear and Transfer

One of the most important problems in the study of the mechanism of wear is the production of wear particles. Most of the previous work which deals with wear has been focused on the rupture or the breakdown of a fragment from its original surface, but little work has been carried out on the behavior of the fragment from its origin to its removal from the rubbing system as a wear particle. Kerridge and Lancaster (73) have found that the fragments sheared from their surface are removed as wear particles only after first adhering to the opposite surface. Cocks (74) and Antler (75) have observed, microscopically, the formation process of wear particles from the adhered fragments between the mating surfaces. Sasada, using X-ray microanalysis, has found mutual transfer in dry sliding (76,83), as well as in lubricated systems (84). Moreover, transfer in polymer systems was reported by Sasada (85). These observations have shown that a wear particle is not a fragment which is produced from its original surface through rupture process, but is one that involves processes which are not yet well known between the rubbing surfaces.

The mechanism of formation of wear particles proposed by Sasada (76) involves a cycle which includes formation, growth and removal of the transfer particles. It is summarized below:
(1) A "transfer element" is formed when a small fragment of either surface portion is sheared off and adheres onto the mating surface. A metal-metal junction is formed at the contact of asperities and is sheared by the frictional force.

(2) A "transfer particle" is formed by the accumulation of "transfer elements".

(3) Through repetition of such an accumulating process, the transfer particle will grow large enough to support the load and be depressed and flattened by frictional motion.

(4) The flattened particle continuously grows in thickness until it is removed by a mechanical impulse from the opposite surface.

Sasada (86) developed a device to observe directly the growth process of the transfer particle and measure the thickness of the particle just before it is removed. With different combinations of mating material, he found that the thickness of the particle is related to the mutual solubility of these two mating materials. For those combinations whose mutual solubility is high, the particle is thicker than for those whose mutual solubility is low. No detectable transfer particle thickness can be measured for the metal combinations such as Mo-Cu, Mo-Ag, Fe-Ag or Ni-Ag in which the metals have poor mutual solubility.
Based on these findings Sasada concluded that the wear particles are produced not from the parent surfaces directly, but through a process of accumulation of numerous minute fragments derived from the parent surfaces.
Chapter III

3 EXPERIMENTAL PROCEDURE

3.1 Wear Testing Machine

A standard $\alpha$-LFW-1 wear testing machine purchased from Faville Levally Corp. was used in this investigation. The machine was modified by V. Shende (91). Modifications included a controlled atmosphere chamber, and a simple wear debris collector. Additionally, a thermocouple was attached to the test specimen for continuous measurement of temperature.

The standard $\alpha$-LFW-1 is shown in a schematic diagram in Fig. 3-1. Basically, it is a block-on-ring wear machine containing (1) a rigid shaft on which the ring is held by friction (2) a specimen holder to hold the test block (3) a counter balanced (to damp oscillations) compound lever with a 30 : 1 loading ratio. The shaft can rotate at speeds ranging from 0-900 rpm. The specimen holder is directly connected to a load cell in order to measure the friction (tangential) force.

To control the testing atmosphere, a plexiglass box was fitted to the front of the $\alpha$-LFW-1. Pre-purified argon can be bled into the box near the bottom, and air is pushed
Fig. 3-1 Schematic representation of LFW-1
(Taken from Ref. 91)
out through holes at the top of the box. Once the desired atmosphere (20% relative humidity) is obtained the holes at the top are sealed with putty.

Debris collector is made by three plexiglass sliding trays. The three sliding trays are arranged parallel to the sliding direction, immediately below the ring. These trays can be withdrawn by strings attached to them, and run through a small hole in the cover of the atmosphere box. Therefore, debris from different duration of times can be separately collected by withdrawing the sliding trays.

The load cell and the thermocouple are connected to a chart recorder (Houston Instrument Omnigraphic 3000) to monitor the friction coefficient and the temperature rise due to friction. Frequent calibration of the chart recorder is needed to obtain accurate data.

3.2 Wear Testing Procedure

This section describes the procedure used to perform wear tests by the LFW-1 wear machine. Reproducibility of the results is an important consideration for a wear test. Factors that affect the reproducibility may be summarized as followed:

(1) Careless or unstandardized cleaning procedure for both the block and the ring. Fischer(118) has recommended that the specimen should not be tested until the surface was clean enough to wet a drop of water.
(2) Badly positioned test block. The block should be perfectly aligned so that the load is evenly applied to the block.

(3) Uncalibrated chart recorder which yields a false output.

(4) Unstandardized atmospheric condition. Dry Argon atmosphere was kept at 20% relative humidity at all times during these tests.

(5) Unaligned load cell and uncalibrated transducer amplifier.

Good care should always be taken to prevent these factors from affecting the results.

The detailed standard procedure for running the wear tests is described below:

(1) The ring and block were carefully cleaned in an ultrasonic cleaner, using trichloroethylene and methanol bath sequentially. After drying, the samples were weighed on an analytical balance to an accuracy of 0.1 mg.

(2) The specimen holder, the shaft, debris collector and adjacent regions were cleaned with a jet of compressed air and with methanol.

(3) The hemispherical cap was placed on the block and the cap surface was lubricated with Molykote. Gloves were worn to handle the block and ring to prevent contamination.
(4) The block and the cap were mounted in the hemispherical socket below the block holder. The block was supported with the left hand while setting the ring on the tapered shaft with the right hand. Then the ring was tightened with a flat washer and nut.

(5) A 15 lbs (6.8 kg) load was applied on the block, (i.e., 1/2 lbs on the bale rod), and the set screws were tightened at each end of the block holder (do not overtighten). The load was then removed to check that the block was seated flat against the ring.

(6) The height of the knife edge was adjusted so that the lever arm was horizontal when the load was applied.

(7) The thermocouple and debris collectors were in mounted position, and the cover of the environmental chamber was attached.

(8) Prepurified argon was passed into the chamber at an initial flow rate of 30 Cu.ft/hr. The flow rate was decreased to 10 Cu.ft/hr. when a relative humidity of 20% was achieved. The relative humidity was maintained at 20% during the test by adjusting the Ar flow rate.

(9) The X-Y recorder was calibrated by a variable DC power supply with an output range of 0-10 mv. The "gain" and "cal" screws located at the bottom surface of the x-y recorder were adjusted if necessary.

(10) The transducer power supply for the load cell was turned on about 20 minutes before the test began. The
RPM scale was set at 650, (equivalent to a sliding speed of 5cm/sec), and both pens of the x-y recorder were set at zero.

(11) When the RH value of the chamber reached 20%, the LFH-1 was considered ready to run. The motor power unit and the chart recorder were turned on, the switch clutch control was turned to the "clutch" position, and the load was applied to the bale rod to start the test.

(12) At the end of the test, the drive was switched back to "brake on", the bale rod removed, and the friction pen zero rechecked.

3.3 Wear Specimen Preparation

3.3.1 Ring Preparation:

M-2 tool steel rings purchased from Faville-Levally Corp. were used in this investigation. They had a diameter of 1.3775 in., a ground face of 0.321 in., and eccentricity between the inner and outer surface was no greater than 0.0015 in.. The reason for choosing M-2 tool steel as a ring material were:

(1) One way of simplifying the characterization of friction and wear is to reduce the amount of transfer from the ring to the test specimens. Since the elements Mo, W and V contained in M-2 are all grainboundary strengthening species, using M-2 rings was therefore expected to exhibit reduced transfer during
sliding (assuming some of these elements are not incorporated in carbides) (87).

(2) The hardness of M-2 tool steel is much higher than that of the test specimens. As a result, the plastic deformation of the M-2 rings during sliding should be much less than in the sample blocks.

As-received rings were rinsed at least three times in trichloroethylene, using an ultrasonic cleaner to remove the protective grease, followed by two rinses in methanol (ultrasonic).

3.3.2 Block Preparation:

Commercial Berylco 25 Cu-Be alloys were used for the block materials. The chemical composition of the alloy is listed in Table (3-1)

Table 3-1

<table>
<thead>
<tr>
<th>Chemical composition of Cu-Be 25 Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
</tr>
<tr>
<td>Wt%</td>
</tr>
</tbody>
</table>

3.3.2.1 Heat Treatment
The heat treatment of the alloys included (1) solution annealing and (2) age hardening. The heat treatment procedures for the two cases are described below:

(1) Solution annealing: Firstly, the specimens were machined to the dimension of 0.63" x 0.41" x 0.26", which was slightly larger than the standard block size of 0.62" x 0.40" x 0.25". Then the blocks were heat treated in vacuum (about 0.001 torr) at 800°C for 1.5 hours, followed by water quench to room temperature. After heat treatment the blocks were ground to standard size to remove all the surface and internal oxidation layer (88), and then wear tested immediately afterwards.

(2) Age hardening: The alloys were heat treated and aged before machining to standard size, in order to prevent the specimen surface from being either surface or internal oxidized. The alloys were solution annealed in vacuum (~0.001 torr) at 800°C for 1.5 hours, water quenched to room temperature, and then aged in vacuum at 280°C for 8 or 24 hours or at 325°C for 30 hours. After the heat treatments, the specimens were machined to the dimensions of standard size using a fly-cutter, since fly-cutting leaves the least subsurface deformation compared with other methods of machining (66).

3.3.2.2 Surface finishing
The blocks were polished on one of the 0.62 x 0.25 in. faces, using an automatic grinder (Buehler, 69-1000 minimat polisher/grinder) in the following sequence:

1. 240 grit SiC, wet;
2. 400 grit SiC, wet;
3. 6 μm diamond paste and polishing oil, on Texmet paper.
4. 3 μm diamond paste and polishing oil, on Texmet paper.
5. 1 μm diamond paste and polishing oil, on Texmet paper.

The polished blocks were then carefully rinsed, using a procedure similar to that used for the rinsing of the ring.

3.4 Examination of Debris

Examination of wear debris is very important for investigations of the nature and the behavior of friction and wear. Information such as the shape, microhardness, thickness, sizes, microstructures and chemistries of debris are of particular interest. Examination could be carried out by using a wide range of equipment, including optical microscopy, Knoop microhardness, scanning SEM/EDAX/WDX, TEM and STEM.

3.4.1 Plating of debris

1. A fully annealed copper plate (about 0.6" x 0.25" x 0.2" size) was used for the substrate. The plate was
electropolished using a phosphoric acid electrolyte (H₃PO₄ : H₂O ratio: 1 : 1; 1.2 V; room temperature; stainless steel cathode) for about 10 hours, such that a containment well about 500 μm deep was formed.

(2) The prepared substrate was placed about 30° inclined in the first stage electroplating solution (17 g NaCN, 11 g CuCN, 7.5 g Na₂CO₃, 500 ml H₂O), as shown in Fig. 3-2. The current (6mAcm⁻²) was turned on before introducing any debris particles. This allowed debris particles to settle through the electrolyte onto the substrate surface.

(3) After 10 minutes plating, the substrate was tilted such that the surface containing debris particles was vertical.

(4) After 1 hour plating in alkaline cyanide solution, a second stage plating was followed by using an acid solution (100 g CuSO₄·5H₂O, 22.5 g H₂SO₄, 0.5 g C₆H₅OH, 500 ml H₂O; 12mAcm⁻²; room temperature; about 100 hours). At least 1.5 mm thick plating was obtained during the stage. The plated debris was considered ready to be sectioned and prepared for further examinations. The plating procedure is shown in a schematic diagram of Fig.3-2.

3.4.2 Optical Metallography
Optical metallography of debris can be achieved by (1) sectioning and polishing the plated debris and

Fig. 3-2 Schematic diagram of the procedure for preparing debris specimen for TEM observation.
(2) Cold mounting the debris with 5 parts of resin and 1 part of hardener mixture. Most micrographs obtained by method (1) are side-views while, on the other hand, most of the micrographs obtained from method (2) are top-views. The etchant used for the metallography was \((\text{HCl: FeCl}_3: \text{H}_2\text{O} = 1: 3: 8, \text{by volume})\). One part of this solution was mixed with one part of Joy detergent to give good control of etching.

3.4.3 Microhardness Measurements

All the specimens used for microhardness measurements were obtained from the plated debris. The advantages of measuring the microhardness of the plated debris are (1) it is more accurate to measure the microhardness from edge sections of debris flakes because the flake thickness was only about 15 \(\mu\text{m}\), and (2) each flake is closely surrounded by plated \(\text{Cu}\). The measurements were done by a Shimadzu microhardness tester, using a Knoop indenter with a 15 gm load and 5 sec loading time.

3.4.4 SEM/EDAX/WDX

A (JEOL, JSN-35C) scanning electron microscope with energy dispersive X-ray (EDAX) analyser and wave length dispersive X-ray analyser (WDX) was used. To examine the shapes and nature of debris, the debris were mounted on a graphite disc, using a graphitic glue to ensure that the de-
bris were held in place and had good electrical contact with the graphite disc.

To analyse the chemistry or to map a selected element in the debris, it is recommended that a sectioned and metallographically polished plated debris specimen be used, because

(1) The specimen, with debris embedded in plated Cu, has a flat surface to eliminate surface roughness effects during EDAX or WDX analysis.

(2) The plated Cu, which is pure Cu, served as a reference standard and yielded true background counts when mapping with WDX.

For WDX analysis, a LiF crystal with a slit size of 300 μm, a potential of 25 kV, and the manual mode of selecting crystal position were used to detect Fe, Co and Cu. Photographs were obtained by using type 52 Polaroid film.

3.4.5 Debris Thickness Measurement

The typical thickness of debris flakes ranged from 10 μm - 25 μm. In order to accurately measure the thickness of debris flakes by SEM, the debris should be placed such that the normal direction of a flake is exactly perpendicular to the electron beam axis, so as to obtain an exact side-view of the flakes. The procedure for specimen preparation is described as followed:
(1) Select at least 30 flakes with typical sizes from a debris collection under a low power stereo-microscope.

Fig. 3-3 Sketches show the preparation procedure for SEM edge views of large debris flakes.
(2) Tape an adhesive copper tape onto a graphite disc with adhesive side up, as shown in Fig. 3-3.

(3) Place each piece of debris flake onto the copper tape with edge pointing upwards, as shown in Fig. 3-3.

(4) Ar sputter coat the specimen with a thin layer of gold.

(5) With the aid of the tilting and rotating stages of the SEM, obtain the exact edge-view of a debris flake at 2000 times and measure the thickness of the flake.

3.4.6 Transmission Electron Microscopy

A Philip EM 300 conventional transmission electron microscope was used in this investigation. Two kinds of techniques for specimen preparation to obtain good thin foils are described here. The first one enables one to obtain a top-view thin foil from a relatively large debris flake, while the second one is to obtain TEM specimens from both large flake and fine powder debris.

3.4.6.1 Preparation for Top-View Foil

(1) Pick up a large flake (larger than 300 μm x 300 μm) under the stereo-microscope, and two discs, each with a slot of 0.2 mm x 1.5 mm in the center.

(2) Carefully place the flake at the center of the slot and apply graphite glue to fix it in place (Fig. 3-4a).
(3) Adhere another slotted Cu disc on top of the first one with the slot perpendicular to the first one and the flake at the center. That is to say,

Fig. 3-4 Preparation for top-view TEM specimen. Jet polishing and ion thinning follow.
fix the flake in between two slotted Cu-discs and make the two slots perpendicular to each other (Fig. 3-4b).

(4) Jet polish the specimen till perforation is obtained, using a Tenupol Struers Jet polisher at 4 volts and room temperature with an electrolyte of 100 g/l CrO₃, 800 ml H₃PO₄ and 300 ml distilled water. The perforation obtained by jet-polishing should be at the edge of the flake due to an edge effect, and the region near the edge of the flake should be thinner than the center region.

(5) Ion thin the specimen at 5 KV gun voltage, 20 μA specimen current and 10° specimen to ion beam angle for about 24 hours. The ion beam should thin the center region faster than the edge region because of the 10° shadow effect to the ion beam. Combining jet-polishing and ion thinning, a good TEM flake specimen can be obtained.

3.4.6.2 Plating, Sectioning and Polishing of Debris

(1) Plate the debris after the wear test, following the procedure described in section(3.4.1).

(2) Spark erode the plated block into 500 μm slices, using a Servomet spark cutter with a cutting speed selector setting of 5 and with Cu wire of 5 mil size.

(3) Adhere the slice onto a specimen holder for mechanical polishing, as shown in Fig. 3-2.
Use 600 grit abrasive paper to polish both sides of the slice mechanically to 150 μm thickness.

(4) Spark erode the slice to form a 3 mm disc, using a Servomet spark cutter at a cutting speed setting of 6. Be sure the interface between the plated and base Cu is right at the center of the 3 mm disc.

(5) Jet polish the disc with the method described in section (3.4.6.1) until a perforation is obtained.

(6) If needed, ion thin the specimen to enlarge the area that is transparent to the electron beam.

2.4.7 Scanning Transmission Electron Microscopy

The specimen preparation procedures for STEM are the same as the procedures for TEM. The STEM used was a JEOL 200CX model (at United Steel Co. Pittsburgh, PA). Most of the STEM work was focused on micro-micro diffraction of the fine grains in debris. The size of the incident beam was about 100 Å.

3.5 Examination of Blocks

3.5.1 Wear Surface

After the wear test, the wear scar was first examined by SEM (JEOL, JSM-35C). Of particular interest were the scar size, wear surface morphology, amount of Fe transfer, distribution of transferred Fe, and morphologies of the built-up material near the entrance & exit ends. In some cases, a
wear surface was examined twice, i.e. before and after ultrasonic cleaning in methanol.

3.5.2 Subsurface Microstructure and Chemical Analysis

3.5.2.1 Cu Plating

The block was electro-chemically plated with copper to protect the wear surface. A two-stage plating procedure was used. The first stage involved the use of an alkaline cyanide solution (17 g NaCN, 11 g CuCN, 7.5 g Na₂CO₃, 500 ml H₂O) for 1 hour at room temperature and 6 mA cm⁻². After that, the second stage plating was followed by using an acid solution (100 g CuSO₄·5H₂O, 22.5 g H₃SO₄, 0.5 C₆H₅OH, 500 ml H₂O; 12 mA cm⁻²; about 100 hours) to produce a plating at least 1.5 mm thick. A stream of lab air was bubbled over the specimen during the entire plating event to give a more uniform Cu deposit (Fig. 3-5).

3.5.2.2 Sectioning

All sections for the purpose of TEM investigation were done with a Servomet spark cutter (at cutting selector setting #5, and with 5mil size Cu wire). Thin slices 500 µm thick were cut in either longitudinal or transverse section, as shown in Fig. 3-6a and Fig. 3-6b. For optical metallography or SEM observations, sections can be done by a LECO, Vari/cut VC-50 diamond cutter, but care should be taken to ensure that during cutting, the stress on the wear scar is
Fig. 3-5 Diagram shows the preparation procedure for TEM observation of section of wear block.

- **Plating**
- **Sectionning**
- **Mechanical polishing**
- **Spark eroding to 3 mm disk**
- **Jet polishing**
- **Ion thinning**
Fig. 3-6 Diagram shows the longitudinal, transverse and taper sections.
compressive (89) in order not to damage the plating interface. The diamond cut-off wheel was used at low speed with Isocut lubricating oil.

The method for preparing a taper section specimen is shown in Fig. 3-6c. Basically, it utilizes the curved nature of the scar. The specimen after plating was mechanically polished from the top surface down toward the bulk, the angle of the taper section can be calculated from the width of the plated Cu that still remained on the surface after polishing, as \( \theta = \sin^{-1}(d/2R) \) where \( d \) = length of plated Cu still remained, \( R \) = ring radius = 1.75 mm (see Appendix A)

3.5.3 Optical Metallography

3.5.3.1 Mounting

The plated sections were mounted in standard 1" mounts, using a room temperature cure epoxy (5 parts Buehler #20-8130 plus 1 part Buehler #20-8132). This mounting method was selected to avoid heating the wear samples during conventional Bakelite pressure/heat processes.

3.5.3.2 Polishing

The procedures for mechanical polishing are described as follows:

1. 400 grit SiC paper with running water.
2. 6 \( \mu \)m diamond and polishing oil on Texmet paper.
3. 3 \( \mu \)m diamond and polishing oil on Texmet paper.
(4) 1 μm diamond and polishing oil on Texmet paper.
(5) 0.3 μm alumina and a few drops of water on microcloth.
(6) 0.05 μm alumina and a few drops of water on microcloth.

At stages 1-4 heavier pressure may be applied to prevent the interface from rounding or being damaged (90). At stages 5 and 6 only light pressure was applied, and the time of polishing was less than 1 min. A prolonged polishing may result in a contaminated surface, or a damaged interface. In addition, it is important to thoroughly clean the specimen with trichloroethylene or methanol after each step to remove all the polishing particles which are larger than the ones used in the next step.

In some cases, electro-polishing was needed to improve the quality of the specimen. An Aardvark Instrument Model V potentiostat, with a reference electrode of potassium chloride solution was used. The electrolyte and polishing conditions were: phosphoric acid and water, 1 : 1 by volume, and 1.25 volts at room temperature.

3.5.3.3 Etching

The composition of etchant is given below:

\[ 39\% \ FeCl_3 : HCl : H_2O \]

\[ = 1 : 3 : 8 \ by \ volume \]
As in section (3.4.2), the solution was mixed with Joy detergent to give a solution having controlled etching rate. Experience showed that the etching times used are quite different for the transfer layer and the bulk material; usually 5-10 sec. were appropriate for good etching of the transfer layer and about 30 sec. were used to etch the bulk material.

3.5.3.4 Microhardness Measurements

Microhardness measurements were made prior to etching for all three kinds of sections, because an etched specimen might cause false microhardness readings. A knoop indenter with 15gm load and 5 sec. loading time was used so that a single indentation can be made within the transfer layer. The microhardness tester used was a Shimadzu microhardness tester type M.

3.5.3.5 SEM, EDAX, and WDX

The polished specimens could be examined in SEM either with or without etching. For an etched specimen, good secondary electron images could be obtained without difficulties, but for an unetched specimen, it is suggested to use a higher condenser lens current (i.e., adjust the condenser lens knob counterclockwise) in order to obtain better secondary electron images. However, the highly condensed beam may contaminate the specimen.
To quantitatively analyse the chemistry of a specimen, EDAX is more efficient than WDX. Computerized EDAX analysis based on comparing the counts per second of X-rays detected by a solid state X-ray detector, and the Z.A.F. (Atomic #, absorption and secondary fluorescence, respectively) corrections enable us to quantitatively detect small amounts of transferred Fe. However, for qualitative mapping of an element of interest, WDX is much more effective and sensitive than EDAX. A LiF crystal detector was used to map the elements from K - Sr by varying the crystal heights, either manually or automatically.

One disadvantage of WDX mapping is that the mapping can not be made at magnifications lower than 200X, because the electron beam had to be highly condensed when using WDX and, thus, the electron beam couldn't cover an area large enough for mapping.

It is worthwhile to provide data here for the penetration depth of the electrons and for the effective zone which produces X-rays. An example is shown in Fig. 3-7

Copper and copper based alloys are between Al & Au, and the effective zone is estimated to be about 1.2 μm.

3.5.3.6 TEM/STEM

The procedures for the preparation of TEM specimens are described as followed(Fig. 3-5):
Fig. 3-7 Monte Carlo calculations of electron trajectories and X-ray production. (a) Electron trajectories - 20 kv electrons in gold; (b) electron trajectories - 20 kv electrons in aluminum; (c) X-ray production - 20 kv, AuKα; (d) X-ray production - 20 kv, AlKα. (courtesy of Wells (126))
(1) Spark erode the plated block into thin slice of 500 um thickness.

(2) Mechanically polish the slice using 400 grit SiC, (wet) and 6 um diamond in polishing oil, using a specimen holder described in Fig. 3-5, section 3.5.3, until the thickness is about 150 um.

(3) Spark erode the slice into 3mm discs. The interface between the plating and the specimen should be at the center of the disc. Make sure that the disc is small enough to be fitted in the TEM specimen holder.

(4) Jet polish the specimen (same electrolyte as in section 3.4.6.1) using a Struers jet polisher at 4 volts and room temperature. In order to get a better chance of having the perforation at the region near the interface, a two-step polishing method was used:

(a) Adjust the specimen such that the interface is about 0.5mm below the center of the hole specimen holder and the plating is at the upper half. Polish for about 2 minutes.

(b) Readjust the specimen such that the interface is about 0.5mm above the center and polish for about 4 minutes until a perforation is obtained, as shown in Fig. 3-8

Experience showed that the polishing rate of the bulk was faster than that of the plating, therefore, an even polishing between the bulk and the plating would result in a perforation at the plating, which was not favored.
Fig. 3-8 Two-step jet polishing the specimen for TEM observation. (a) interface 0.5 mm above the jet axis for 2 minutes, (b) interface 0.5 mm below the jet axis until perforation is obtained.
(5) After a perforation is obtained, quickly rinse the specimen in successive baths of distilled H2O and methanol. Since methanol reacts with the phosphoric acid, the rinsing in distilled water should be careful and thorough.

(6) If necessary, ion thin the specimen further to enlarge the area of the electron-transparent region, using a potential of 5 KV and a specimen current of 2 μA until a suitable foil is obtained (Edwards Model 306 specimen preparation unit equipped with an IBT 200 ion beam thinning accessory). Routine examination of the foils was conducted on a Philips EM300 TEM fitted with a double-tilt goniometer stage and operating at 100 KV. Additional high magnification imaging and micro-microdiffraction were done on a JEOL 200CX STEM.

3.6 Examination of Coated Material on Ring

After the wear test, a layer of Cu colored block material was always found to be coated on the ring surface. SEM examinations on the surface morphology of the layer were conducted with the JEOL, JSM-35C. After that, a plating technique described below was used for the purpose of further EDAX/WDX and TEM examination.

(1) Plate the ring with the same acid and alkaline baths and current densities as those described in section 3.4.1. The ring is held horizontally by 3 Cu
wires, as shown in Fig. 3-9. The ring is connected to the "-" output of a power supply. Both the bubbled air and magnetic stirrer are used to ensure that the agitation was effective on all of the ring surface. Plating is stopped when the plating thickness was about 0.5mm, i.e. after about 1/2 hours in the alkaline bath and 24 hours in the acid bath.

(2) Mechanically polish the front and the rear faces, as shown in Fig. 3-9, to remove all the plated Cu on those two faces.

(3) Make two cuts on the remaining plating, with a distance of about 3cm in between, and peel the section off. The coated transfer material should be attached to the plating after this peel-off.

(4) Replate the section with the same procedure as described in step (1) until the plating thickness was at least 5mm. The plated sample could then be further processed for EDAX, WDX or TEM examinations by the same procedures described in sections 3.4.
Fig. 3-9 Procedure for plating and sectioning the ring coating.

Plating the ring after wear test.

Peeling off the plating after making two cuts (arrows).

Replacing the ring coating.

SECTION
Chapter IV

4. EXPERIMENTAL RESULTS

4.1 Microstructures of the Alloys After Heat Treatment

As mentioned earlier, the primary goal of this investigation was to study how the precipitates affect the friction and wear in Cu-Be alloys. Therefore, microstructural examination of the specimen before wear testing was needed to allow comparison with information obtained during and after sliding tests.

The grain size of the specimen was about 50 μm, for all heat treatments used. An example is shown in Fig. 4-1, which is an optical micrograph of a specimen aged at 280°C for 8 hours. In addition to the small precipitates, which were too small to be revealed by optical microscope, some large Co-containing particles were also found.

TEM observations of the precipitation sequence are shown in Fig. 4-2. The heat treatments of these specimens were solution annealing, and aging at 280°C for 8 hrs. or 24 hrs., or at 325°C for 3 days. All the diffraction patterns were taken from exact <001> orientations to reveal the precipitate spots at different stages. No precipitate spots or spikes along <100> directions were found in the solution.
Fig. 4-1 Optical micrograph of a fully age-hardened specimen. Dark spots are Co-contained particles, which were heavily etched during electropolishing.

Fig. 4-2a (001) diffraction pattern of a solution annealed specimen. Kikuchi pattern shows that the beam is parallel to one of the <001> zone axis.
annealed specimen, Fig. 4.2a, but extensive Kikuchi lines were observed. In contrast, spikes along <100> directions and precipitate spots at 2/3(200) showed up at 8 hrs. aging (Fig. 4-2b), and, as the aging continued, the spikes vanished and each precipitate spot split into two small spots (Fig. 4-2d, 4-2b, 4-bf, 4-2h). Furthermore, Kikuchi lines could not be found in any of the age hardened specimens. TEM images, (Fig. 4-2c, e, g, i) showed that the size of the precipitates increased as the aging time increased (20, 21). The differences between the diffraction patterns of solution annealed and age hardened specimens have been emphasized because these differences might provide information to determine how the precipitates were changed as a result of sliding.

The results of microhardness measurements on specimens with different heat treatment is shown in Table 4-1

Table 4-1

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Microhardness (KHN) (15g, 5 sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution annealed</td>
<td>90</td>
</tr>
<tr>
<td>280°C 6 hrs. aging</td>
<td>360</td>
</tr>
<tr>
<td>280°C 8 hrs. aging</td>
<td>370</td>
</tr>
<tr>
<td>280°C 24 hrs. aging</td>
<td>330</td>
</tr>
<tr>
<td>325°C 30 Hrs. aging</td>
<td>310</td>
</tr>
</tbody>
</table>
Fig. 4-2b (001) diffraction pattern of a fully-age hardened specimen.

Fig. 4-2c TEM image of the fully-hardened specimen.
Fig. 4-2 d (001) diffraction pattern of a specimen aged at 280°C for 24 hours.

Fig. 4-2 e TEM image of the specimen aged at 280°C for 24 hours.
Fig. 4-2 f (001) diffraction pattern of specimen aged at 280°C for 3 days. ppt. spots are fan shaped.

Fig. 4-2 g TEM image of specimen aged at 280°C for 3 days.
Fig. 4-2h (001) diffraction pattern of specimen aged at 325°C for 3 days. ppt. spots split into two spots, and no spikes along <200> direction can be seen.

Fig. 4-2i TEM image of the specimen corresponding to Fig. 4-2h
It can be seen that a maximum value was obtained after 8 hrs. aging at 280° C, and the hardness is decreased with continued aging to the lowest value after 3 days aging at 325° C.

4.2 Wear Test Results

Steady state average friction coefficients and loose debris weight generated per hour are presented in Table 4-2. In order to have a closer examination of the effect of heat treatment on friction and wear, the friction and wear data are plotted as a function of aging in Fig. 4-3 (a,b), and as a function of microhardness in Fig. 4-4(a,b). In terms of friction data, fully hardened specimens, H1, tend to give lower friction values. The friction coefficients increase with either increasing or decreasing the aging time. As for the wear loss, it can be seen that the solution annealed specimens have the lowest wear loss. As aging continued, the wear loss increases to a maximum for fully hardened specimens and then slightly decreases for overaged specimens.

As shown in Fig. 4-4, it seems that both friction coefficients and wear losses vary significantly when the specimen hardnesses are greater than 300 KHN. The reason for such drastic change may be attributed to the relative hardness values of the transfer layer and the bulk, (1). This will be discussed in Chapter 7.
<table>
<thead>
<tr>
<th>specimen</th>
<th>KHN</th>
<th>debris weight/hr.</th>
<th>friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15lb.</td>
<td>30lbs.</td>
</tr>
<tr>
<td>H0: #46</td>
<td>116</td>
<td>2.18mg</td>
<td>0.59</td>
</tr>
<tr>
<td>#39</td>
<td>95</td>
<td>2.06mg</td>
<td>0.68</td>
</tr>
<tr>
<td>#34</td>
<td>96</td>
<td>0.94mg</td>
<td>1.7mg</td>
</tr>
<tr>
<td>H1: #50</td>
<td>371</td>
<td>1.52mg</td>
<td>0.57</td>
</tr>
<tr>
<td>#42</td>
<td>365</td>
<td>5.06mg</td>
<td>0.59</td>
</tr>
<tr>
<td>#41</td>
<td>368</td>
<td>3.66mg</td>
<td>0.57</td>
</tr>
<tr>
<td>#35</td>
<td>375</td>
<td>1.27mg</td>
<td>4.35</td>
</tr>
<tr>
<td>#40</td>
<td>371</td>
<td>1.47mg</td>
<td>0.59</td>
</tr>
<tr>
<td>H2: #60</td>
<td>330</td>
<td>3.13mg</td>
<td>0.66</td>
</tr>
<tr>
<td>#161</td>
<td>335</td>
<td>1.33</td>
<td>0.65</td>
</tr>
<tr>
<td>H4: #24</td>
<td>306</td>
<td>3.79</td>
<td>0.66</td>
</tr>
<tr>
<td>#23</td>
<td>309</td>
<td>3.88</td>
<td>0.68</td>
</tr>
<tr>
<td>#27</td>
<td>298</td>
<td>1.32</td>
<td>2.28</td>
</tr>
</tbody>
</table>
Fig. 4-3a Friction coefficient vs. heat treatment. The friction coefficient is obtained by averaging data measures from different tests at steady state. Typical scatter for friction coefficients was ±0.05.

- ■: 30 lbs. (13.6 kg) load
- □: 15 lbs. (6.8 kg) load
Fig. 4-3b Results of wear data from different heat treated specimen.
- ■: 30 lbs. (13.6 kg) load
- ◼: 15 lbs. (6.8 kg) load
Fig. 4-4a Results of friction data plotted against specimen hardness.

x: 30 lbs (13.6 kg) load
o: 15 lbs (6.8 kg) load
WEAR VS. KHN

Fig. 4-4b Results of wear data plotted against specimen hardness.

x: 30 lbs (13.6 kg) load
o: 15 lbs (6.8 kg) load
All friction traces of age hardened specimens were noisy and unstable, even though the rings were not damaged during the test. An example is shown in Fig. 4-5, which is a section of the friction trace for a fully hardened specimen (run # 49).

On the contrary, friction traces of solution annealed specimens were less noisy and stable at steady state. Fig. 4-6 shows a typical friction trace for a solution annealed specimen. It is seen that the friction rises to about 1 during the initial 15 minutes and then gradually levels off to the steady state value thereafter. The shape of the friction trace shown in Fig. 4-6 is consistent with results of Jellinson (59).
Fig. 4-5 A section of the friction trace of run #49. The specimen was fully age hardened (run #49, 30 lbs. 2 hrs.).
Fig. 4-6 The friction trace of run #46 with 30 lbs. load for two hours. The specimen was solution annealed.
Chapter V

5. MICROSTRUCTURAL EVALUATIONS

This section describes observations of the microstructural features in test blocks, debris and the coated transfer material on rings. Optical microscopy, SEM/EDAX/WDX, Auger, TEM and STEM have been used in making these observations. In addition, microhardness tests were performed on polished sections in the near-surface regions, and these data are included.

5.1 Examination of Solution Annealed Specimens

Scanning electron microscope examination showed that the wear surface for the solution annealed specimen was relatively smooth. A typical SEM picture is shown in Fig. 5-1. It is quite clear from Fig. 5-1 and Fig. 5-2 (a higher magnification of Fig. 5-1 near the exit side) that pieces of debris have traveled across the surface, plowing out grooves as they went. Fig. 5-2 shows two such particles retained at the exit side of the wear scar. They are pressed into the surface due to the relatively low hardness of the alloy for this heat treatment.

Transverse sections of this specimen, Fig. 5-3a, Fig. 5-3b, show that the subsurface microstructure of the region
Fig. 5-1 SEM image of the wear scar of a solution annealed wear specimen (run #36), sliding direction is pointing downward.

Fig. 5-2 Magnified SEM image of the exit side in Fig. 5-1.
Fig. 5-3a Transverse sectioned optical micrograph of the same specimen as in Fig. 5-1. The section position is near the entrance side. Large Co-containing particles are seen, but no cracks are evident.

Fig. 5-3b Transverse section view of the region near exit side of Fig. 5-1. The specimen is more heavily etched than the specimen in Fig. 5-3a.
near the entrance side is quite different from that near the exit side. Fig. 5-4a, b and Fig. 5-5a, b are SEM images and Fe WDX maps of the regions near the entrance and exit side, respectively. It can be clearly seen that transfer (Fe) was only detected near the entrance side. The shape of the transfer layer is curved and like an array of cylindrical sections, with the cylinder axes parallel to the sliding direction. Although the wear surface near the exit side is grooved, there is no transfer layer observed in that region. The material just below each of these grooves seems to be deformed more heavily than other areas. Since no transfer layer is involved in the dark etching layer in Fig. 5-5, that layer is believed to be generated purely by high subsurface plastic deformation.

Earlier work by P. Heilmann (94) has shown that transfer layers tend to build up first at the entrance side, because that is where debris or the transfer material from the ring coating tends to accumulate prior to being swept into (and across) the interface. At longer times, the transfer layer spreads gradually across the interface until steady state conditions are attained. In addition to the difference in chemistry between the transfer layer near the entrance side and the highly deformed layer near the exit side, the microstructures of both layers are also different, although their geometries look similar. From the optical micrographs of Fig. 5-3a, b, it is clear that the transfer layer has
Fig. 5-4a SEM image of the transverse section in Fig. 5-3.

Fig. 5-4b Fe WDX map corresponding to Fig. 5-4a.
Fig. 5-5a SEM image of the specimen in Fig. 5-3b (Transverse section near the exit side).

Fig. 5-5b Fe WDX map of Fig. 5-5a.
flow line features associated with it, while the highly deformed layer hasn't. Results of further TEM examination on that difference will be provided later.

The microhardness values of both the transfer layer and the material underneath it are of particular interest in this investigation. Fig. 5-6a, b, show the micrograph of the Knoop hardness indentations and KHN-distance plot, respectively. The average microhardness of the transfer layer is about KHN 260, whereas that of the block is about KHN 125. Note that the hardness measured is slightly larger than values of the as-quenched specimens, which are about KHN 100, because aging might have taken place during the wear test and during the specimen preparation period.

The material just below the transfer layer, the highly deformed layer, has a hardness of about KHN 200. This value is harder than the corresponding layer in OFHC Cu wear specimens (92). This indicates that the work hardening rate of the solution annealed Cu-Be alloy is higher than that of the OFHC Cu due to the large amount of Be solute present. This could be due to twinning, or, possibly, some precipitation might have taken place during sliding.

Fig. 5-7 is a TEM picture of a transverse-sectioned specimen. The transfer layer is found on the very top of the wear surface. Just below it is the highly deformed layer which contains elongated cells. The original grain
Fig. 5-6a Microhardness indentations of the transfer layer as well as the substrate. Note the transfer layer is harder than the base.

Fig. 5-6b Microhardness value vs. subsurface distance plot. The substrate hardness falls with distance from the surface.
Fig. 5-7 TEM image of the transverse sectioned wear specimen from a solution annealed wear test. Upper right is plated Cu. The specimen was tested with a 30 lbs. load for 2 hours.
boundaries have disappeared as they approach the highly deformed layer. This finding is similar to the work of P. Heilmann (102).

Further below the wear surface, both deformation twins and dislocation structures are observed. To confirm that they are twins, a selected area diffraction pattern associated with a bright field and a dark field image from the area indicated by the arrow in Fig. 5-7 are provided by Fig. 5-8a, b, c.

Fig. 5-8a is an (011) diffraction pattern. Since (011) is an invariant vector between the twin and the matrix, therefore, the (011) diffraction patterns of the matrix and the twins will be superposed with each other on an (011) diffraction pattern, and each twin spot is located at the position where the corresponding matrix spot is rotated 70.5° about (011). As a result, each twin spot will be displaced by 1/3[111] along a [111] direction and the twin spots will be coincident with the matrix spots in every three rows. This is exactly what is found in Fig. 5-8a. The twin images can be further revealed by the dark field technique, as shown in Fig. 5-8C. The dark field image is taken from the (111) twin spot indicated by the arrow in Fig. 5-8a. It should be noted that some streaks along the (111) twin plane are also observed in Fig. 5-8a. These streaks are due to the shape effect (120) from the fine deformation.
Fig. 5-8a (011) selected area diffraction pattern of Fig. 5-8b. A twin spot is indicated by the arrow.

Fig. 5-8b Bright field image of the region about 7 µm below the wear surface (the region is indicated by an arrow in Fig. 5-7). Both dislocation structures and deformation twins are evident.
Fig. 5-8c Dark field image of the same area in Fig. 5-8b. The exciting twin spot is the arrowed spot in Fig. 5-8a.

Fig. 5-9 TEM image of an area about 12 \( \mu \text{m} \) below the wear surface. Regularly oriented striations are observed.
twins. The details of indexing and calculating the twin spots have been provided in Appendix B. It is interesting to point out that at least four twin systems were found in the left grain of Fig. 5-7. These four twin systems accompanied by dislocations are sufficient to satisfy the Von Mises criterion which states that there should be at least five slip systems in order to be compatible for the deformation of polycrystalline material.

According to W. Bonfield (35), the first observable feature of the decomposition of the supersaturated Cu-Be solution was the appearance of regularly oriented markings in the grains, referred to as striations, along the traces of \{110\} planes. Such striations are also observed in Fig. 5-9, which is an area about 12 \( \mu \text{m} \) below the wear surface. This indicates that some precipitation might have taken place during the sliding.

The twin density decreases as the distance from the wear surface increases. At about 20 \( \mu \text{m} \) below the wear surface, dislocations seem to be dominant. However, equiaxed dislocation cells such as those found in OFHC Cu (92) were not found. This indicates that the stacking fault energy of Cu-Be alloy is lower than that of OFHC Cu due to the 13at.\% Be solutes. The dislocation structure at about 25 \( \mu \text{m} \) below the wear surface is shown in Fig. 5-10.
Fig. 5-10 TEM image of the region about 25 μm below the wear surface. Dislocation structures dominate, but they do not form well-defined cells.

Fig. 5-11 TEM image of a longitudinal sectioned specimen. Note smooth flow around particle and absence of cracks or crack nuclei near the particle.
In some cases the highly deformed layer was thicker than the one shown in Fig. 5-7. As shown in Fig. 5-11 a highly deformed layer containing elongated cells is thicker than about 10 μm. Also, the cell spacings increase gradually with increasing distance from the surface. The large inclusion in Fig. 5-11 contains cobalt, which was added to stabilize the alloy (95). It should be noted that the material around it flows like a fluid around a rock in a stream, and no fracture is evident.

For better understanding of the microstructural response to plastic deformation, TEM pictures of the cold rolled solution annealed specimen are provided in Fig. 5-12a,b. These show the microstructures after 40% and 80% reduction of area, respectively. It is clear that extensive twinning is observed in Fig. 5-12a but not in Fig. 5-12b. This fact may provide the explanation for the observation of Fig. 5-7. Well-defined deformation twins can only be found at a certain region below the wear surface. Very close to the wear surface, elongated cell structures dominate. This also implies that deformation twinning itself cannot accommodate large strains, e.g., larger than 80% reduction of area. Ruff (96) has also pointed out that deformation twinning was important during erosion tests. However, deformation twins could only be found in the material between about 1 μm and 5 μm from the impact surface. According to Ruff (96), immediately below the surface, where the deformation is most
Fig. 5-12a TEM image of the solution annealed specimen after cold rolling of 40% reduction of area. Both deformation twins and dislocation structures are seen.

Fig. 5-12b The specimen was cold rolled 80% reduction of area, showing extensive dislocations but no deformation twins.
intense, the twins are no longer distinct and a fine grained polycrystalline layer is observed. Furthermore, in the region below the deformation twins, a well-developed dislocation cell structure is present. Ruff's findings are consistent with Fig. 5-7.

A TEM picture of the transfer layer is presented in Fig. 5-13. Ultra-fine grains, about 50-300 Å size, are observed in the transfer layer. The selected area diffraction pattern, Fig. 5-14, shows that in addition to the Cu diffraction rings, faint Cu₂O and BeO rings are also detected. No precipitate ring is seen in Fig. 5-14. Fig. 5-15 is a micro-micro diffraction pattern taken from a single grain in the transfer layer. The (011) diffraction pattern shows that the crystal is quite perfect. No streaks along the <200> directions are found, which indicates that no precipitate is present in the transfer layer.

5.2 Examination of Age Hardened Specimens

The wear scar morphology and the subsurface microstructures of the age hardened specimens are drastically different from those of the solution annealed specimens.

It is believed that precipitates play a very important role in causing such differences. The results of microstructural studies are presented below.
Fig. 5-13 Transverse section TEM view of the solution annealed specimen. The transfer layer stays on the wear surface.

Fig. 5-14 Selected area diffraction pattern of the transfer layer in Fig. 5-13. Faint oxide rings are detected.
Fig. 5-15 Micro-microdiffraction pattern of a single grain in transfer layer. The beam axis is an \( <011> \) direction. The crystal is nearly perfect since the spots are not split.
Generally, the wear surface of an age hardened specimen is rough compared with the solution annealed case. Fig. 5-16 is an SEM picture of a typical wear surface for aged Cu-Be alloys. The surface is rough and irregular with plateau-like features of various sizes and shapes rising about 15 um above the surface. Higher magnification views of these plateaus showed many cracks near the edges, indicating that some of the wear debris flakes were generated by fracture of plateau edges. Examples of these cracks are visible in Fig. 5-17.

Chevron patterns (97,98) were usually found on the plateau surface (see Fig. 5-18). They were spaced ranging from about 2 to 10 um. Some were sharply pointed and some were smoothly curved. Different rows were concave in opposite directions on the same plateau.

Fig. 5-19 is an optical micrograph of a transverse-sectioned specimen which shows a dark layer of material, i.e., plateau or transfer layer, above the surface level of the substrate material rather than pressed into it as in the case of solution annealed specimens. A crack is found at the interface between the plateau and the substrate, this crack actually extended to the edge of the plateau but part of the crack near the edge was filled by plated Cu.

The microhardness, the chemistry and the microstructure of plateau material are very different from those of
Fig. 5-16 SEM image of the wear surface of a fully age hardened wear specimen, showing the rough wear surface containing surface plateaus. The wear test was done with a 30 lbs. load (13.6 kg) for 2 hours.
Fig. 5-17 SEM image of a region near a plateau edge. The test loads were 30 lbs. (13.6 kg) for 1 hour and 45 lbs. (20.1 kg) for 1 hour.
Fig. 5-18 Chevron pattern of the plateau surface. The sliding direction is pointing downward. The specimen aged at 280°C for 24 hrs., and tested at 30 lbs. (13.6 kg) for 1 hr. and 45 lbs. (13.6 kg) for 1 hr.

Fig. 5-19 Optical micrograph of transverse section of an aged Cu-Be test block (30 lbs. load (13.6 kg), 2 hrs.). The plateau is elevated about 15 μm above the base material.
the substrate. It is also striking that the debris was found to be very similar to plateau material in terms of micro-hardness, chemistry, microstructure and thickness. The results of debris examination will be presented later in Section 5.3.

Fig. 5-20a,b show an SEM image and a WDX Fe map, respectively. It can be clearly seen that the transfer layer is softer than the substrate. The hardness of the transfer layer is about KHN 250, while that of the substrate is about KHN 370. As a result, the "soft" transfer layer could not be pressed into the harder base material (1). The WDX Fe map of Fig. 5-20b shows that Fe is uniformly distributed throughout the transfer layer. According to EDAX analysis, the amount of transferred Fe was about 0.5 wt%.

To reveal the plastic deformation of the substrate, longitudinal sections might serve better than transverse sections (see Fig. 5-21), because thin curved features such as the twin boundaries in Fig. 5-21 provide information on how the substrate responds to sliding plastically. Again, the substrate surface is flat and the transfer layer occurs as elevated plateaus.

In order to examine the optical microstructure of each plateau and to match the micrograph of each plateau with the corresponding one observed by SEM, a taper section technique described in section 3.5.2.2. was used. Basically it
Fig. 5-20a Microhardness indentating of the specimen in Fig. 5-4. Block material was too hard for the transfer layer to be pressed into it.

Fig. 5-20b Fe WDX map corresponding with Fig. 5-5a. Transfer layer contains about 0.5 wt% Fe from the M2 ring.
Fig. 5-21 SEM micrograph of longitudinal section of an over aged specimen (280°C, 24 hrs.). Transfer layer remained on the surface.
utilized the curved nature of the wear scar and polished directly downward on the plated wear surface. Fig. 5-22 shows an SEM image of such a taper-sectioned specimen. The central band marked with "p" is the plated Cu and both sides show bulk material. The transfer layer would show up earlier than the substrate during polishing since it is higher than the substrate. Comparing Fig. 5-16 and Fig. 5-22, it is clear that each of the white regions in Fig. 5-22 corresponds with the plateau at the same location in Fig. 5-16. It is interesting to note that the thickness of the plateau in Fig. 5-16 can be calculated with the aid of Fig. 5-22, as

$$T = W \times \sin \sin^{-1} \left(\frac{d}{2R}\right)$$

where
- $T =$ thickness of plateau
- $W =$ length of the chosen section of transfer layer along the sliding direction
- $d =$ width of the plated Cu, which is 1.1 mm for the case shown in Fig. 5-22.
- $R =$ radius of the ring = 17.5 mm

For example, for the plateau indicated by an arrow in Fig. 5-16, the calculated thickness is 18 µm which agrees with Fig. 5-19. The development of Eq. (5-1) is explained in Appendix (A).

To examine the metallography of the transfer layer, a magnified optical picture of one of the sections of transfer layer material shown in Fig. 5-22 is presented in Fig. 5-23.
Fig. 5-22 SEM micrograph of taper section of the specimen in Fig. 5-16. Each white area corresponds to the plateau at the same position in Fig. 5-16.
Fig. 5-23 Optical micrograph of the taper section shown in Fig. 5-7, showing flow features in transfer layer. Note that some particles are not yet pressed firmly.
Flow features were usually found in the transfer layer material. In addition, some loose particles which had not been pressed firmly during sliding are observed in Fig. 5-23. Generally, it is more likely for those loose particle regions to be found near the bottom of plateaus, though some loose particles near the edge do not seem to be pressed firmly together. The mechanism for the formation of plateaus is believed to be very similar to that for mechanical alloying. Benjamin, et al (99,100,101), have pointed out that flow features are observed after mechanical alloying aluminum and magnesium particles.

If the specimen is heavily etched the subsurface microstructure of the substrate can be revealed. Fig. 5-24 shows that the substrate material twins extensively during sliding. TEM evidence of twinning will be presented later.

Microhardness measurements on taper-sectioned transfer layers as well as on the substrate might be helpful in providing information on the variation of hardness with depth, although they might not be very precise due to thickness effects. However, the general trend of hardness with depth should be revealed. Fig. 5-25, a, b show the microhardness indentations and the KHN vs. depth plot. It can be seen that the microhardness stays constant near the wear surface and then decreases when it is close to the interface between the transfer layer and the substrate. The microhardness of
Fig. 5-24 Optical micrograph of the heavily etched taper section. Deformation twins are revealed in the substrate material.
Fig. 5-25a Microhardness indentations of taper sectioned specimen. The transfer layer near the interface is loose and soft.

Fig. 5-25b Microhardness vs. distance plot. The distance is not the true subsurface depth, but it can be converted to the true distance.
the substrate immediately below the transfer layer is about KHN 400, which is much harder than the transfer layer. The low hardness values of the transfer layer near the interface are believed to be due to the presence of relatively loosely pressed particles. If the transfer material had been firmly pressed and sheared, the microhardness should be about KHN 300.

Chemical analysis for oxygen has been conducted by Scanning Auger spectroscopy. Before Auger data were obtained, the specimen was Ar ion-bombarded in the chamber to ensure an ultra-clean surface. Fig. 5-26a, b shows the secondary electron image and the oxygen Auger electron map of the same transfer layer as the one shown in Fig. 5-25. The oxygen line scan of that transfer layer is shown in Fig. 5-27. Oxygen and iron are uniformly distributed throughout the transfer layer. TEM examination, which will be described later, shows that that the oxygen is in the form of oxide with the particle size of about 50 μm.

The results of TEM observations are presented in the following section. A number of successful thin foils allowed the Author to

(1) identify twins and index twinning directions.
(2) demonstrate the absence of subsurface dislocation cell structures.
Fig. 5-26a SEI image taken by Scanning Auger Spectroscope of the taper sectioned plateau.

Fig. 5-26b Oxygen Auger electron map of the same area as in Fig. 5-11b. The specimen was cleaned by Argon sputtering thoroughly before mapping.
Fig. 5-27 Oxygen Auger electron line scan of the specimen in Fig. 5-26. Three line scans were made at three positions.
(3) determine the microcomposite nature of transfer layers which contain fine metal particles and oxides but no precipitates.

(4) study the whole spectrum of the subsurface microstructures.

Fig. 5-28a shows a TEM picture of a region about 18 μm below the wear surface. Extensive deformation twinning is found, but no dislocation cell structures are observed. A selected area diffraction pattern associated with Fig. 5-28a is shown in Fig. 5-28b. The selected area aperture covered both twin systems as well as the matrix; therefore, two sets of twins are detected at exactly the position where they should be. (see Appendix B). In addition to the twin spots, Fig. 5-28b also shows streaks along <200> directions indicating the presence of early stage precipitates. Dark field images from the two twin spots are provided in Fig. 5-29a, b. They were imaged from g spots indicated by arrow a and arrow b, respectively. It should be noted that the electron gun was tilted such that the g's were perpendicular to the optical axis. The twin direction <211> is consistent with ordinary twin directions in FCC crystals.

It is clear from Fig. 5-28a and Fig. 5-29b that at least four twin systems were active in the grain. However, those four twin systems are not sufficient to satisfy Von Mises compatibility criterion which requires at least five deformation systems. The possible explanations are:
Fig. 5-28a TEM bright field image of a region 18 μm below the wear surface. Together with the dark field images (Fig. 5-29), this picture shows at least four twin systems in this area.

Fig. 5-28b Selected area diffraction pattern associated with Fig. 5-18a. Two sets of twin spots are identified. Spikes along <200> direction are also evident.
Fig. 5-29a Dark field image taken from the exciting g spot indicated by arrow a in Fig. 5-28b. Note that the electron gun was tilted such that \(-g\) was coincident with the optical axis.

Fig. 5-29b Dark field image from the twin spot indicated by arrow b in Fig. 5-28b. Twin directions are consistent with the normal FCC twin directions.
(1) Earlier work by P. Heilmann (102) has shown that the rotation of the subsurface cells about the Z axis (Normal to wear surface) is very small. As a result, four major deformation systems might satisfy the compatibility criterion.

(2) It should be difficult to find all five systems in a three dimensional space by viewing a "two" dimensional foil within a small area. The TEM foils are very thin, about 2000 Å.

(3) The possibilities of dislocation motion and grain boundary sliding can not be ruled out completely. Grain boundary sliding might even be possible if the deformation twin density near the grain boundary is higher than near the matrix, as shown in Fig. 5-30.

The twin density increases when it is closer to the surface (See Fig. 5-30). Also, twins are bent toward the sliding direction. In Fig. 5-31, which is a dark field image at higher magnification, one set of deformation twins can intersect another system of twins, causing visible offsets.

When they are very close to the surface, deformation twins are further distorted and the volume fraction of twins is about the same as in the matrix. An example is shown in Fig. 5-32a, b, which show a TEM image and an (011) selected area diffraction pattern at about 2 μm below the wear surface. The twin and the matrix spots have the same intensity,
Fig. 5-30 TEM image of the microstructure 2 µm below the surface. Twin density is high; also, twins are tilted toward the sliding direction.

Fig. 5-31 Dark field image of twinned microstructure. One twin system is intersected by another set of twins, causing visible offsets.
Fig. 5-32a TEM image of region 2 μm below wear surface. Twins are heavily deformed.

Fig. 5-32b Diffraction pattern of region similar to the area shown in Fig. 5-16a. Twin spot intensity is about the same as the matrix spot intensity. All spots are extended.
and both are split indicating that they are rather extensively deformed.

Fig. 5-33a, b, shows the TEM image at the interface and the diffraction pattern of the transfer layer. It can be seen that the transfer layer contains ultra-fine particles and the diffraction pattern shows Cu$_2$O and BeO extra rings. However, precipitate rings were absent. If the precipitate rings did exist the first precipitate ring should have a radius of 2/3 of the copper (111) ring radius. The microstructures, the chemistry and the microhardness of the transfer layer are very similar to those of the debris. Therefore, details of the TEM analysis of the transfer layer may be referred to in section (5.3).

5.3 Debris Analysis

Since debris particles originate in the interface region of a sliding pair as a result of frictional deformation, examination of debris to correlate the nature and the microstructure of the debris and the test specimen is important for wear studies. Debris have been studied previously by numerous investigators. In some cases, the size and shape distributions of debris particles were of interest (103). Some work has also dealt with the elemental composition of debris (144). In lubricated systems various methods of extracting debris from the lubricant have been developed and put into practice (105,106). For TEM observations
Fig. 5-33a TEM image of the interface between transfer layer and the base. The microstructures of the two materials are drastically different.

Fig. 5-33b Diffraction pattern of the transfer material. Faint oxide rings are clearly seen, but no precipitate ring is detected.
some good techniques (93) for preparing thin foils were employed. These enabled researchers to obtain detailed structural and chemical information about the debris. Furthermore, Sasada (7-14) has recently published a series of papers emphasizing the importance of mutual transfer found in debris as well as on the wear scar.

In this investigation detailed microstructural and chemical information has been obtained by using optical microscopy, SEM, TEM, STEM and fluorescence analysis using energy dispersive techniques (e.g., EDAX) and wavelength analysis (WDX). The results show a clear connection between the generation of loose wear debris and the transfer layer.

5.3.1 General Character of the Debris

The data presented in this section have been arranged to provide a general picture, e.g. shape and morphology, of the debris based on optical and SEM observations. Usually, two kinds of debris were collected from tests of age hardened specimens, i.e., flake-like debris and fine powder debris. Fig. 5-34 is an SEM picture of a debris collection which shows that the flake-like debris ranged from about 50 μm to 500 μm and the resolvable fine debris are about 0.5 - 10 μm. However, due to the limitation of SEM resolution and the difficulties of collecting and distinguishing very small debris, the possibility of the presence of powdered debris smaller than 0.5 μm can not be ignored.
Fig. 5-34 SEM image of debris from fully hardened specimen wear test (30 lbs., 2 hrs.).

Fig. 5-35 Debris collection from the test of solution annealed specimen. The test was done by 30 lbs. for 2 hrs..
Fig. 5-35 is a typical SEM picture of debris collected from a solution annealed specimen test. Less fine debris were found, while, in contrast to the age hardened case, some layered debris particles were collected in addition to flake. The layered debris usually have wedge shapes in side-view as shown in Fig. 5-36. Earlier work by P. Heilmann (94) has suggested a "finger extrusion" mechanism to explain generation of layered debris at the exit side of the wear track. Since no evidence for extruded fingers was found in this investigation, it is suggested that the layered debris were generated from the entrance side. The morphology of the layered debris was similar to that of the built-up material near the entrance side (e.g., Fig. 5-37). It is very unlikely that such layered debris could be generated in the wear track and still remain unchanged in shape after removal.

When viewing debris collections by SEM or optical microscope, scratches were found on almost all the flake debris. This suggests that both sides of a single flake should have scratches. In Fig. 5-38a, Fig 5-38b, both sides of a single flake were examined. It is clearly seen that indeed both sides of the flake are grooved. Furthermore, those scratches in Fig. 5-38a and b are parallel to each other which indicates that both surfaces may have experienced sliding, one at a time, before the particle moved out as a loose debris particle. Based on these observations,
Fig. 5-36 Same as Fig. 6-2, but a magnified side-view of a layered debris.

Fig. 5-37 The built-up material near the entrance side of a solution annealed wear specimen. The test were: 30 lbs., 2 hours.
Fig. 5-38a The upper surface of a debris flake. The surface contains scratches and Chevron markings. The test block was overaged (325°C, 3 days).

Fig. 5-38b The lower surface of the same flake as in Fig. 5-38a. The scratches are parallel to the upper ones.
A theory has been developed to calculate the flake thickness by using the energy-based friction model (7), which will be presented in section (6.1). An edge-view of the flake in Fig. 5-38 is shown in Fig. 5-39. The thickness of the flake is about 16 μm. The two perpendicular fracture surfaces look different, indicating that those two surfaces had experienced different fracture processes before the flake was generated.

Debris flakes could be mounted and etched for optical examination. An example of one such flake is shown in Fig. 5-40. The internal structure of the flake appears to be the same as that of the transfer layer in Fig. 5-3 and Fig. 5-23, i.e., the flow features are similar in both pictures.

Chemical analyses by EDAX and WDX provide further evidence of the connection between the debris and the transfer layer. According to EDAX, transferred Fe in debris was about 0.5 wt%. The SEM image and WDX map of Fig. 5-41a,b show that the transferred Fe was rather uniformly distributed throughout the debris, although a few localized iron particles were found occasionally. The debris was plated with pure Cu, therefore the Fe WDX map should be reliable. The specimen surface was flat and the plated Cu provided a convenient reference standard for the background level.

5.3.2 TEM Examination
Fig. 5-39 Edge-view of the flake in Fig. 6-4. The two edges are nearly perpendicular to each other.

Fig. 5-40 Optical micrograph of a cold mounted flake. The debris was a little tapered. It is seen that the "flow feature" resembles the transfer layer and the transfer material was not firmly pressed near the lower right portion of the picture.
Fig. 5-41a SEM micrograph of plated debris.

Fig. 5-41b Fe-Kα X-ray map (WDX) corresponding to Fig. 5-41a.
As mentioned earlier, transfer material contains ultra-fine Cu grains and oxide particles. TEM examination of debris also showed the same structures. Fig. 5-42 is a typical example of a side-view of flake debris substructure. It can be seen that the grain size is about 50-300 Å, just as it was in the transfer material. The grains are equi-axed, i.e., no significant difference was found between side-view and top-view TEM pictures (See Fig. 5-43). The corresponding diffraction pattern is shown in Fig. 5-44. The results of analysis of Fig. 5-44 revealed that the debris structures were mixed-crystals of fine and relatively randomly oriented FCC Cu, Cu₂O and BeO phases, as shown in Table 5-1. No precipitate of any phase was detected. The d-spacings of all the precipitate phases of interest are listed in Appendix (C).

It should be pointed out that no difference was found throughout the entire thickness of a flake debris particle from the TEM side-view picture. No substrate material containing precipitates and deformation twins was observed near either surface, i.e., evidence of delamination of substrate material was not observed. Fig. 5-45 shows examples of TEM side-view picture near both interfaces between the plating and the debris. Fine powder debris were also plated and observed in TEM; they have the same fine structure as the larger flakes (see Fig. 5-46).
Fig. 5-42 Side-view TEM picture of a flake. The flake was plated, sectioned and jet-polished.

Fig. 5-43 Top-view TEM picture of a flake, using the technique described in Section 3.4.6.1. The flake was Argon ion thinned for 20 hours after about 1 minute jet polishing.
Fig. 5-44 Selected area diffraction pattern of a flake. Oxide rings are detected, but no precipitate ring is seen.

Table 5-1

Indexing of the diffraction pattern in Fig. 5-44

<table>
<thead>
<tr>
<th>R (mm)</th>
<th>d (Å)</th>
<th>reflecting plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.2</td>
<td>2.436</td>
<td>Cu₂O(110)</td>
</tr>
<tr>
<td>12.9</td>
<td>2.30</td>
<td>BeO (101)(020)</td>
</tr>
<tr>
<td>13.75</td>
<td>2.161</td>
<td>BeO(120) or Cu₂O(200)</td>
</tr>
<tr>
<td>14.55</td>
<td>2.049</td>
<td>Cu(111)</td>
</tr>
<tr>
<td>16.75</td>
<td>1.774</td>
<td>Cu(200)</td>
</tr>
<tr>
<td>20.25</td>
<td>1.472</td>
<td>Cu₂O(220)</td>
</tr>
<tr>
<td>22.25</td>
<td>1.335</td>
<td>BeO(031) (002)</td>
</tr>
<tr>
<td>23.7</td>
<td>1.258</td>
<td>Cu(220)</td>
</tr>
<tr>
<td>27.75</td>
<td>1.075</td>
<td>Cu(311)</td>
</tr>
<tr>
<td>28.5</td>
<td>1.046</td>
<td>Cu(222)</td>
</tr>
</tbody>
</table>
Fig. 5-45a Side-view TEM image of a flake near one of the interfaces. The upper right portion was plated Cu.

Fig. 5-45b Side-view TEM image of the same flake as in Fig. 6-11a, but near the other interface. No microstructural difference throughout the entire thickness.
Fig. 5-46 TEM image of powdered debris. The debris particle is about 0.5 \( \mu \text{m} \) size. The larger grains are part of the copper plating.
In order to isolate the oxide particles from the Cu grains to examine their sizes and distribution, the dark field technique was used. The results are presented in Fig. 5-47. Fig. 5-47a is the selected area diffraction pattern of part of the area shown in Fig. 5-47b. The dark field image taken from region 1 of the Cu (111) ring is shown in Fig. 5-47c. Fig. 5-47d shows the dark field image taken from region 2 of the Cu2O (111) ring. It is obvious from Fig. 5-47 that the particle size of the oxide is about ten times smaller than that of the Cu grain. These oxide particles are believed to be produced by crushing the thin oxide layer formed when the bare Cu was exposed to the atmosphere during the blending and pressing process. This indicates that the process is similar to mechanical alloying (99, 100, 101).

Co was added to the alloy as a stabilizer to aid grain refinement. It has been reported (28) that Co reduces the precipitation rate, and suppresses the discontinuous reaction until about 380°C. After sliding, large particles rich in Co were found in debris as well as in the test specimen. These Co particles were almost undeformed in both the debris and in the test block. Fig. 5-48 shows such a Co particle embedded in the transfer material. No significant microstructural difference was found around the circumference of the particle, as was found in Fig. (5-48). Using X-ray microanalysis in STEM, Williams (95) pointed out that those particles contain both Co and Cu and in fact appear to
Fig. 5-47a Selected area diffraction pattern of the debris flake from an aged specimen test.
Fig. 5-47b Bright field TEM image associated with Fig. 5-47a.
Fig. 5-47 c Dark field image of the Cu(111) ring in Fig. 6-13a, with the objective aperture positioned at region "1".

Fig. 5-47 d Dark field micrograph showing Cu₂O or BeO diffracting to region "2" of Fig. 6-13a.
Fig. 5-48 TEM image showing a "cobalt" particle embedded in the debris structure. The particle was nearly undeformed.

Fig. 5-49 Selected area diffraction pattern of Fig. 5-48. The selecting area aperture was slightly larger than the "Co" particle. No diffracting ring is consistent with "Co" particle diffraction.
to scavenge the Fe and Si trace impurities also. In addition to those elements detected by Williams, Bonfield (108) claimed that those particles contained Be. Due to the complexity and uncertainty in the chemistry of the "Co" particles, direct indexing of the diffraction pattern to trace the "Co" diffraction rings is very difficult. However, an easier way to check whether there are "Co" rings in a diffraction pattern is presented in Fig. 5-49. The selected area diffraction pattern was taken from the area which covered both the particle and the transfer material. It can be clearly seen that no ring is consistent with the "Co" particle's single crystal diffraction pattern. This indicates that the particles were not crushed into very fine ones during the sliding events.

In order to provide further evidence that precipitates were absent from the debris (or the transfer layer), convergent beam microdiffraction and micro-microdiffraction techniques were employed. Fig 5-50 is a convergent beam microdiffraction pattern from a 500Å grain in a debris particle. Clear Kikuchi lines could be seen, which indicates that precipitates have disappeared, because, as mentioned in section (4.1), Kikuchi lines can only be observed in solution annealed specimens (relatively perfect, unstrained crystals). Fig. 5-51 shows micro- microdiffraction pattern taken from a 200 Å grain in the debris. By comparing with the (001) diffraction pattern of the age hardened specimen in
Fig. 5-50 Converging beam diffraction pattern from a grain about 500 Å size in the debris. Clear Kikuch pattern implies that the grain is free from precipitate.
Fig. 5-51 Micro-microdiffraction pattern taken from a single grain in the debris structure. The beam axis is <001> direction. No precipitate spots are found at 2/3<200> copper spots.

\[ \lambda L = 5.730 \text{ mÅ} \]
section (4.1), it is evident that no precipitate is in the Cu grains.

It is interesting to mention here that quite extensive twinning was found within the fine Cu grains. Fig. 5-52 shows STEM image of debris at a magnification of 1,000,000 times. Micro-twins with dimensions of about 10-20 Å were present in a grain as small as 200 Å. Fig. 5-53, an (011) micro-microdiffraction pattern, provides the proof that they are indeed twins. Extra twin spots were found rotated about matrix (011) zone axes by 70.5° and displaced by 1/3 [110] along [111] direction in every three rows, just as described in section (5.2).

Effort has also been made to find out the form in which the transferred Fe exists. Fortunately, a single crystal piece of iron was located by using the micro-microdiffraction technique, as shown in Fig. 5-54. Since both Fig. 5-54 and Fig. 5-51 are operated under the same condition (i.e., same camera constant and electron wave length), the diffraction pattern of Fig. 5-54 can be indexed by calculating the (camera constant) x (wave length) value from the (001) Cu pattern of Fig. 5-51. The result shows that Fig. 5-54 is a bcc (111) pattern with a lattice spacing of 2.8 Å, which is in good agreement with α-iron. The details of the indexing are also provided in Fig. 5-54a.

5.4 Examination of the Coated Transfer Material on the Ring
Fig. 5-52 High magnification STEM image of debris showing ultra-fine twin (about 20 Å) in the copper grain.

Fig. 5-53 (011) micro-microdiffraction pattern of a single grain in debris, showing the evidence of twins. Note actually two sets of twin spots are observed in the diffraction pattern.
Fig. 5-54 Micro-microdiffraction pattern of a bcc grain in debris structure. By carefully calibrating the camera constant ($\lambda X L$), the pattern is indexed as bcc Fe (111) diffraction.
During each of the wear tests, the M-2 ring surface becomes partially coated by transfer material in a few minutes. The coating is copper colored at the beginning. As the sliding time is increased, it gradually changes to a brown color with increasing thickness. At steady state, the coating seems to reach a constant amount, but its thickness is varied at different positions and at different times. In general, the amount of coating is less when a smooth wear surface is obtained on the block, and it is greater when the wear surface is rough.

The transfer material coated on the ring surface was plated by using the technique described in section (3.6), and then sectioned for SEM or TEM analysis. A typical example of the SEM image is shown in Fig. 5-55. Although the ring coating is about 5 µm according to Fig. 5-55, its true thickness may be greater because some of the material may be lost during the plating and peeling procedure. The Fe WDX map corresponding with Fig. 5-55 is shown in Fig. 5-56. Again, transfer Fe is detected and is uniformly distributed.

TEM and STEM studies showed that the ring coating had a microstructure similar to that of the transfer layer and the debris. Fig. 5-57 is a TEM image for the ring coating of test #50 with a fully hardened test block. No obvious microstructural difference is seen across the entire thickness. The ultra-fine grained nature is strikingly similar
Fig. 5-55 SEM image of the ring coatings which is sandwiched between plated Cu.

Fig. 5-56 Fe-K\textsubscript{\alpha} X-ray map (WDX) of the same region in Fig. 6-18.
Fig. 5-57 TEM image of the transfer material coated on the ring surface showing the structure similar to debris and transfer layer.

Fig. 5-58 High magnification TEM picture of the ring coatings. Note the microcomposite nature of the material and the micro-twins in the grains.
to both the transfer layer and the debris. In a magnified TEM image, e.g., Fig. 5-58, it is clearly seen that the grain size is about 50-300Å and that the fine grains contain micro-twins. Fig. 5-59 is a selected area diffraction pattern corresponding to Fig. 5-57. No precipitates were detected in the material. The microcomposite nature is again evident, the structure consists of fine grains of Cu and oxides of Cu and of Be.
Fig. 5-59 Selected area diffraction pattern of Fig. 5-58. Cu$_2$O and BeO are detected, but no precipitates are found.
Chapter VI

6. THEORETICAL APPROACH

This section describes two theories developed by the author to explain two phenomena found by microstructural observations. The first one is to predict the thickness of flake debris collected from tests of age hardened specimens, and the second one is to explain the morphology of the transfer layer in solution annealed wear specimens. Both calculations are extensions of Heilmann's and Rigney's Energy-based friction model.

6.1 Calculation for Flake Thickness Prediction

6.1.1 Summary of Experimental Observations:

The experimental findings relevant to this calculation may be summarized as follows:

1) Both sides of a debris flake have scratching grooves and these grooves are parallel. This implies that both surfaces of a flake may have experienced sliding before it came off. However, it should be pointed out that the grooves may also be the "replica" of grooves on base material surface that is formed earlier.
(2) Plateaus were found above the substrate. These were flat and had the same thickness and microhardness as debris flakes, but they were softer than the substrate.

(3) Microstructural studies showed that the structures and chemistry (e.g., transfer Fe or oxides) of the plateau and the debris are similar.

(4) Cracks were usually found at the interface between plateau and substrate. Top views of plateaus also showed evidence of cracks near the edge.

(5) Transfer material was always found coated on the ring surface. This material had structure and chemistry similar to that of the plateau and debris.

(6) Taper sections of wear specimens showed that the transfer material near the interface was loose and soft. Plateaus may be formed by blending and pressing a pile-up of small particles (see section (5.2)). Some region of the interface was not strongly bonded.

6.1.2 Basic Assumptions:

Based on the findings described in the preceding section, a simplified diagram (Fig. 6-1) was drawn to show the relative geometry of the ring, the block and the transfer layer. With the geometry of Fig. 6-1 in mind, one can define a friction coefficient (µ₁) at interface 1 when interface 1 is sliding, i.e., when the plateau is not moving.
Fig. 6-1 Schematic diagram showing the geometry of the plateau, the ring coating and the block.
Similarly a friction coefficient \( \mu_2 \) can be defined at interface 2 when the sliding is on interface 2, i.e., when the plateau is carried by the rotating ring. Therefore the condition to determine whether the plateau is ready to be moved out of the interface region so that it may become a loose debris particle can be found by the relative values of \( \mu_1 \) and \( \mu_2 \). When \( \mu_1 \) is greater than \( \mu_2 \), then the plateau is considered ready to be removed, because whichever interface is sliding should be determined by the one which has a lower friction coefficient.

As mentioned in section (2.8), the energy-based friction model predicts that the friction coefficient varies as the coating thickness is varied. Similarly, \( \mu_1 \) and \( \mu_2 \) are also functions of plateau as well as ring coating thickness.

6.1.2.1 Derivations of \( \mu_1 \) ---sliding on Interface 1

There are three contributions to the total plastic energy to be considered, namely, the energy associated with the base, with the plateau and with the ring coating. These are represented by \( W_{PL}^B \), \( W_{PL}^P \), \( W_{PL}^C \), respectively. In order to simplify the calculation, some further assumptions were made. They are summarized as follow:

1. The stress was assumed to be constant throughout the transfer material of both plateau and ring coating. Since the strain in the transfer material was very high, therefore there was little work hardening for the
transfer material. The stress-strain curve could essentially be assumed to be levelled off at high strains. Furthermore, the microstructure of the transfer material was found to be composed of very fine grains, i.e., about 50-300 Å. It is reasonable to assume that there are no work hardening effects in such fine-grained material because grain-boundary sliding, or fine grain flowing, might be the dominant deformation mechanism.

(2) The ring coating thickness was assumed to be similar to the plateau thickness. Due to the experimental difficulties in measuring the ring coating thickness, no evidence has been found to support this assumption at this point. However, this assumption is not absolutely necessary in the calculation. Ring coating thickness can be treated as a variable, as will be described in section 7.2.

(3) The transfer layer was assumed to have no structural gradient across the thickness.

(4) The structures and properties of the plateaus and the coating on ring were assumed to be the same.

According to the energy-based model, $W^\rho_{PL}$, $W^c_{PL}$ and $W$ can be written as

$$W^P_{PL} = NA \int_0^T \tau \Delta \gamma dz = W^c_{PL}$$  \hspace{1cm} (6-1)

$$W^P_{PL} = NA \int_0^\infty \tau \Delta \gamma dz$$

$$= NA L_{\tau_{\text{max}}} \delta X_s \exp(-a_{\tau} L) P(\tau_I/\tau_{\text{max}})$$  \hspace{1cm} (6-2)
Assuming the stress in transfer material to be constant and equal to $\tau_{max}$,

$$W_{PL} = W^P_{PL} + W^C_{PL} + W^B_{PL}$$

$$= 2NA^L \tau_{max}^L \delta X_s [1 - \exp(-a^L T)]$$

$$+ NA^L \tau_{max}^L \delta X_s \exp(-a^L T) F(\tau_I/\tau_{max})$$

where $\tau_I$ is the stress at the interface, which should be equal to $\tau_{max}$ if the stress in transfer material is constant, and terms associated with a superscript $L$ represent parameters for the layer of transfer material. Therefore, an expression for $\mu_I$ can be found by using $W_F = W_{PL}$ and the correction function $f(T)$. The result is

$$\mu_I(T) = \{1 - f(T)\} \frac{(NA)^L}{L} \{2 \tau_{max}^L [1 - \exp(-a^L T)] + \tau_{max}^L \exp(-a^L T) \cdot F(\tau_I/\tau_{max}) + f(T) \} \frac{NA}{L}$$

$$\tau_{max}^L F(\tau_s/\tau_{max})$$

6.1.2.2 Derivation of $\mu_2$---sliding on interface 2

The plastic work term of the transfer material above interface 2 (see Fig. 6-1) can actually be treated as a "soft-coated-on-soft" case (note that the transfer material is softer than the substrate). Therefore, similar to the calculation in section (6.1.2.1), the plastic work above interface 2 is given by $W^P_{PL} = W^C_{PL}$. Thus
\[ W_{PL}^p + W_{PL}^p \]
\[ = (NA)^{L'} \tau_{max}^L \delta x_s^L \left[ 1 - \exp(-aLT) \right] \]
\[ + (NA)^{L'} \tau_{max}^L \delta x_s \exp(-aLT) \left[ 1 - \exp(-aLT) \right] \]
\[ = (NA)^{L'} \tau_{max}^L \delta x_s \left[ 1 - \exp(-2aLT) \right] \]  
\[ \text{6-5} \]

where \((NA)^L'\) is the contact area at interface 2.

It is interesting to point out that if the plastic work term above interface 2 is treated as the plastic work in the transfer material with thickness of 2T (i.e., plateau plus coating thickness), the result will be exactly the same as Eq. (6-5).

The plastic work below interface 2 can be found simply by calculating the plastic work of an uncoated system with the surface stress of \(\tau_{max}'\), since the surface stress at interface 2 should not be greater than \(\tau_{max}'\), the maximum shear stress of the transfer material. That is to say, a hard material cannot be deformed by a soft material by a stress which is greater than the maximum shear stress of the soft material. Therefore,

\[ \frac{W_{PL}^B}{(NA)^L} \tau_{max}^L \delta x_s F\left(\frac{\tau_{max}}{\tau_{max}}\right) \]
\[ \text{6-6} \]

when Eq. (6-5), Eq. (6-6) and the correction function \(f(T)\) are combined, the result for \(\mu_2\) is

\[ \mu_2(T) = \left(1 - f(T)\right) \frac{(NA)^L}{L} \left[ \tau_{max}^L \delta x_s F\left(\frac{\tau_{max}}{\tau_{max}}\right) \right] \]
\[ + \tau_{max}^L \left(\frac{\tau_{max}}{\tau_{max}}\right) + f(T) \frac{(NA)}{L} \tau_{max}^L \delta x_s F\left(\frac{\tau_s}{\tau_{max}}\right) \]
\[ \text{6-7} \]
6.1.3 Results of $\mu_1$, $\mu_2$ Calculations:

Eq. (6-4) and Eq. (6-7) can be further simplified by normalizing both equations by $\frac{(NA)^L}{\tau_{\text{max}}}$, because $\frac{(NA)^L}{\tau_{\text{max}}} = \mu_L$ is not a function of $T$. By doing so, $\mu_1$ and $\mu_2$ can be rewritten as

$$\mu_1 = \frac{\mu}{u_L} \{1 - f(T)\} \left[\frac{(NA)^L}{(NA)^L} \right] \left[2 \cdot \left[1 - \exp(-a^L_T)\right]\right] + \frac{\tau_{\text{max}}}{\tau_{\text{max}}} \exp(-a^L_T) F(\tau_{\text{max}}/\tau_{\text{max}})$$

$$\mu_2 = \frac{\mu}{u_L} \{1 - f(T)\} \left[\frac{(NA)^L}{(NA)^L} \right] \left[\frac{\tau_{\text{max}}}{\tau_{\text{max}}} \exp(-2a^L_T)\right] + \frac{\tau_{\text{max}}}{\tau_{\text{max}}}$$

$$+ \frac{f(T)^L}{(NA)^L} \frac{\tau_{\text{max}}}{\tau_{\text{max}}} \frac{\tau_{\text{max}}}{\tau_{\text{max}}} F(\frac{\tau_{\text{max}}}{\tau_{\text{max}}})$$

The contacting area at interface 1 should be about equal to that at interface 2, because the top and bottom surface areas of a debris flake are similar and there are no microscopic differences in those two surfaces. Therefore, $\frac{(NA)^L}{(NA)^L}$ should be equal to 1. Furthermore, considering steady state friction, $\frac{\tau_{\text{max}}}{\tau_{\text{max}}}$ is then equal to 1. Now the only parameters left in Eq. (6-8) and Eq. (6-9) in addition to $T$ are $\frac{(\tau_{\text{max}}^L)}{(\tau_{\text{max}}^L)}$ and "a", which are all material properties.

Up to this point Eq. (6-8) and Eq. (6-9) are ready to be examined. A computer program has been set up to calculate the $\mu_i$ value; and allow easy comparison. (see Appendix (D) for program). One of the results is shown in Fig. 6-2 (parameters are $a = 0.07 \mu m^{-1}$, $\frac{\tau_{\text{max}}^L}{\tau_{\text{max}}^L} = 0.6$). Earlier work of
Fig. 6-2 Calculated $\mu'1$ and $\mu'2$ (normalized by $\frac{N^2 - \mu L}{\mu_{mx}}$) plotted against the plateau thickness.
P. Heilmann (102) has shown that \( a = 0.05 \, \mu m^{-1} \) for OFHC Cu. Since the transfer material is harder than OFHC Cu (1), therefore \( a = 0.07 \, \mu m^{-1} \) should be more appropriate for transfer material (note that higher "a" values represent smaller deformation depth). The reason for \( \frac{\tau_{max}}{\tau_{max}} = 0.6 \) is based on the fact that the transfer material hardness is about 0.6 times the substrate hardness.

It is striking that Fig. 6-2 predicts the debris flake thickness to be about 17 \( \mu m \), which is in good agreement with experiments (e.g., Fig. 6-38). At 17 \( \mu m \) \( \mu_1 \) starts to be greater than \( \mu_2 \) and hence the segment of plateau material is ready to move out of the interface region so it can become loose debris.

Since \( \frac{\tau_{max}}{\tau_{max}} \) and "a" are arbitrarily chosen in Fig. 6-2 and no measured quantities are available to use, it is worthwhile to determine how \( \frac{\tau_{max}}{\tau_{max}} \) and "a" affect the result of the calculation. Fig. 6-3 and Fig. 6-4 are the results calculated and plotted by computer (see Appendix (E) and (F) for the programs) for the predicted debris thickness vs. \( \frac{\tau_{max}}{\tau_{max}} \) and the predicted debris thickness vs. "a". It is found that the predicted debris thickness is not very sensitive to \( \frac{\tau_{max}}{\tau_{max}} \) until \( \frac{\tau_{max}}{\tau_{max}} \) is greater than 0.9, while the predicted debris thickness varied from 40 \( \mu m \) to 6 \( \mu m \) as "a" increases from 0.03 to 0.2 \( \mu m^{-1} \). The decay constant is closely related to the depth of the deformation zone, in fact,
Fig. 6-3 Predicted debris thickness as a function of the stress ratio, $\frac{\sigma_{\text{min}}}{\sigma_{\text{max}}}$.
Fig. 6-4 Predicted debris thickness plotted against the decay constant "a".
the inverse of the decay constant represents the depth below the surface where the displacement decays to about 36%, i.e., 1/e of the surface displacement. Therefore, it is clear that the predictions are very satisfactory when reasonable choices are made for the parameters $\frac{\tau_{max}}{\tau_{max}}$ and "a".

According to the preceding calculations, it seems that the debris thickness is largely determined by the decay constant "a". The physical interpretation of the calculation is that sliding at interface 1 will no longer be energetically favored when the transfer layer is thicker than some critical thickness. At the critical condition, the plastic work associated with two transfer layers of thickness T (i.e., plateau and ring coating) becomes higher than the plastic work associated with one transfer layer with thickness 2T. As a result, the system would choose interface 2 as a sliding surface rather than choose interface 1.

Fig. 6-4 predicts that the debris thickness will be increased as the decay constant, a, decreases. Tsuya (9,10) reported that the deformation zone is roughly proportional to (load)$^{+\frac{1}{2}}$. Since the decay constant is actually related to the inverse of the deformation depth, the decay constant should be decreased as the load increases. As a result, Fig. 6-4 also predicts that the debris thickness will be increased when the normal load is increased. Fig. 6-5 shows a plot of the measured debris thickness vs. normal load. It
is found that the prediction of this theory is consistent with the experiments of this investigation.

Fig. 6-5 Measured debris thickness at different load.
6.2 Theory to Explain the Shape of Transfer Layer in Solution Annealed Wear Specimens

In section (5-1), the transverse section of a solution annealed wear specimen showed that the shape of the transfer layer is curved and like an array of up-side-down bumps (see Fig. (5-3)). The transfer material in this case was pressed into the base because it was harder than the base material. A similar morphology has also been found by other researchers (92,109). In this section, the energy-based friction model will be applied to explain the observed morphology. The basic idea of the approach is to compare the total plastic energy associated with a curved transfer layer and the base to the energy associated with a flat transfer layer and the base. The case with the lower energy is assumed to be favored. The author recognizes that this approach will not be correct if the transfer layer shape is determined by kinetic factors instead of by energy considerations.

According to the energy-based model, the total plastic energy of a coated system is

\[
W_{PL} = \delta x_s \{1-f(T)\} (NA)^L \tau_{max}^L \left[ F\left(\frac{\tau_s^L}{\tau_{max}^L}\right) \right] \\
- \exp(-a_T^L F\left(\frac{\tau_I}{\tau_{max}^L}\right)) \tau_{max} \exp(-a_T^L F\left(\frac{\tau_I}{\tau_{max}^L}\right)) \\
+ \delta x_s f(T) (NA) \tau_m^L F\left(\frac{\tau_s}{\tau_{max}^L}\right)
\]

Eq. (6-10) predicts a maximum when T is about 1 \( \mu \)m

The total contacting area, \((NA)^L\), can be converted to

\((NA)^L = M^L \times 1 \times y\)
where $M^L = \text{number of contacts/unit area}$

$l = \text{the length of the wear track}$

$y = \text{the width of the wear track}$

Therefore the total plastic energy per unit sliding distance on the surface, $\mathcal{W}_{PL}/\delta x_s$, can be rewritten as

$$
E = \frac{\mathcal{W}_{PL}}{\delta x_s} = \{1 - f(T)\} M^L \cdot l \cdot y \{\tau_{max}^L [F(\tau_{s}/\tau_{max}^L) \\
- \exp(-a^L_T F(\tau_{I}/\tau_{max}^L))] + \tau_{max} \exp(-a^L_T F(\tau_{I}/\tau_{max}^L)) \}
$$  

6-11

for the uniformly coated systems. However, a nonuniformly coated system, e.g., a curved transfer layer, should be treated differently. Instead of converting $dV$ to $NADz$, the $dV$ term should be substituted by $Mldydz$. The segments of transfer material are assumed here to be long compared with their width. Therefore, the plastic work in the nonuniformly coated layer is

$$
\mathcal{W}_{PL}^L = M^L \cdot l \cdot \int_0^{So} dy \int_0^{T \Delta y} dz \\
= M^L \cdot l \cdot \int_0^{So} dy \delta x_s a^L_{\tau_{max}} \int_0^{T} \{1 - (1 - \tau_{s}^L/\tau_{max}^L)^2 \} \exp(-a^L_L Z) \}^{1/2} \\
\exp(-a^L_L Z) dz \\
= M^L \cdot l \cdot \delta x_s a^L_{\tau_{max}} \int_0^{So} dy F(\tau_{s}/\tau_{max}^L) \exp(-a^L_T F(\tau_{I}/\tau_{max}^L)) \\
$$  

6-12

where $So$ is an arbitrary width of interest in $y$ direction, and $T$ is now a function of $y$ (see Fig. 6-6). The plastic
CASE 1

CASE 2

Fig. 6-6 Schematic diagram showing the geometry of the curved transfer layer, and the flat transfer layer.

Fig. 6-7 Schematic diagram of the assumed two geometry of transfer layer.
work term from the substrate material can be obtained directly from Eq. 2-13 if $\delta x_s \exp(-a^* T)$ is substituted for $\delta x_s$ and $\tau_s$ for $\tau_s$, because the displacement and the stress have to be continuous across the interface. Therefore,

$$W^B_{PL} = M^L \cdot l \cdot \delta x_s \tau_{max} \int_0^{S_i} dy \exp(-a^* T) \frac{P(\tau_s/\tau_{max})}{\tau_{max}}$$

Combining Eq. (6-12), Eq. (6-13) and the correction function $f(T)$, the total plastic energy per sliding distance, $\delta x_s$, for a specimen with width $S_i$ is found to be

$$W^B_{PL} = \int_0^{S_i} dy \cdot M^L \cdot l \left\{ \left[1-f(T)\right] \left[\frac{\tau_s}{L_{max}} F\left(\frac{\tau_s}{\tau_{max}}\right)\right]ight.$$

$$- \exp(-a^* T) \frac{P(\tau_s/\tau_{max})}{\tau_{max}} + \tau_{max} \exp(-a^* T) F\left(\frac{\tau_s}{\tau_{max}}\right)\right\}$$

$$+ f(T) M^L \cdot l \cdot \frac{\tau_{max}}{\tau_{max}} F\left(\frac{\tau_s}{\tau_{max}}\right)$$

Now one can conduct calculations to compare the total plastic energy associated with the two geometries shown in Fig. 6-6 (i.e., case 1 for curved transfer layer and case 2 for flat one). In order to make a fair comparison between the two cases, one has to assume that the total amount of transfer material is the same for both cases, i.e., the shaded areas of case 1 and case 2 in Fig. 6-6 are the same. Furthermore, only one segment of the entire transfer layer with width $S_i$ is needed for calculations. The basic approach of the calculations is to examine how the total plastic energy is varied for both cases as the amount of transfer material is increased. The total plastic energy of case 1 is expected to be lower than the energy of case 2 at cer-
tain range of the transfer layer size. It is mainly due to
the maximum predicted by Eq. (6-10).

6.2.1 Calculations for Case 1

As shown in Fig. 6-7, the shape of the transfer layer
is assumed to be a portion of a circular arc. By varying
the radius of curvature, the size of the transfer layer can
be increased since the width $S_0$ is kept constant. The relation between $t$ and $y$ is

$$t = \sqrt{R^2 - \left( \frac{S_0}{2} - y \right)^2} - \sqrt{R^2 - \left( \frac{S_0}{2} \right)^2} \tag{6-15}$$

Eq. (6-14) can be substituted into Eq. (6-13) to calculate the
total plastic work per sliding distance, $\delta X_s$, by integrating
Eq. (6-13) with respect to $y$. However, Eq. (6-13) is too com-
plicated to be integrated directly. Therefore, the computer
(see Appendix (G) for program) was used to calculate the
area under a $G$ vs. $y$ plot

where

$$G = \frac{3 \left( W_{pl} / \delta X_s \right)}{\delta y} = \frac{\text{plastic work per sliding distance}}{\text{unit width in } y \text{ direction}}$$

$$= M^L \cdot \ell \left[ 1 - f(T) \right] \left[ \tau_{max}^L (\tau_{S}^L / \tau_{max}^L) - \exp(-a^L T) F(\tau_{I}^L / \tau_{max}^L) \right. \left. + \tau_{max}^L \exp(-a^L T) F(\tau_{I}^L / \tau_{max}^L) \right] + M^L \cdot \ell \cdot f(T) \tau_{max}^L F(\tau_{S}^L / \tau_{max}^L) \tag{6-16}$$

In Heilmann's and Rigney's (7) treatment, the transfer ma-
terial, treated by itself as bulk material, would have a $G$
function of

$$G^L = M^L \cdot \ell \cdot \tau_{max}^L F\left( \frac{\tau_{S}^L}{\tau_{max}^L} \right)$$
and without a transfer layer, the base material would give

\[ G^B = M \cdot L \cdot \tau_{\text{max}} F(\tau_s/\tau_{\text{max}}) \]

Using these equations for \( G^B \) and \( G^L \), equation (6-16) becomes

\[ G = [1-f(T)] G^L [1-\exp(-a_L T)] \left\{ \frac{F(\tau_I/\tau_{\text{max}})}{F(\tau_{\text{max}})} - \frac{\tau_{\text{max}} F(\tau_I/\tau_{\text{max}})}{\tau_{\text{max}} F(\tau_{\text{max}})} \right\} \]

\[ + f(T) G^B \]

6-17

The shape of this function depends on the relative values of \( G^L \) and \( G^B \). According to Heilmann and Rigney (7), a maximum occurs when \( G^L /G^B < 1.3 \). Therefore the \( G^L /G^B = 1 \) was used in the calculation. Now the total plastic work can be obtained by using Eq. (6-16) and Eq. (6-14), and calculating the area under the \( G \) vs. \( y \) plot, i.e.,

\[ \frac{W_{\text{PL}}/\delta X_s}{\int_0^{S_0} G dy} = \int_0^{S_0} G dy \]

6-18

Furthermore Eq. (6-16) can be normalized by \( W_{\text{PL}}^0 = G^B \cdot S_0 \), which is the plastic work in the base material without any transfer layer. Thus

\[ \frac{W_{\text{PL}}/W_{\text{PL}}^0}{\delta X_s} = \frac{1}{S_0 \int_0^{S_0} G dy} \int_0^{S_0} G dy \]

\[ = \frac{1}{S_0} \int_0^{S_0} dy \{ [1-f(T)] [1-\exp\left(-a_L T\right)] \left( \frac{F(\tau_I/\tau_{\text{max}})}{F(\tau_{\text{max}})} - \frac{\tau_{\text{max}} F(\tau_I/\tau_{\text{max}})}{\tau_{\text{max}} F(\tau_{\text{max}})} \right) + f(T) G^B \}

6-19
The results of the calculation for case 1 will be presented after the next section, where case 2 is considered.

**Calculation for Case 2**

Since the amount of transfer material is assumed to be the same for both cases, the equivalent thickness of the flat transfer layer, $t'$ in Fig. 6-7, can be calculated from $R$, the radius of the curved transfer layer. The result is

$$t' = \frac{2}{S_0} \left[ \frac{R^2 + 4}{4} - \frac{S_0}{4} R \cos \theta \right]$$

where $\theta = \tan^{-1}\left(\frac{(S_0/2)}{\sqrt{R^2 - (S_0/2)^2}}\right)$  

Combining Eq. (6-19) and Eq. (6-18), the normalized total plastic work can be obtained by calculating the area under the $G$ vs. $y$ curve.

6.2.3 Results of Calculations:

In Eq. (6-18), $\gamma^l_{\text{max}}$ will be larger than $\gamma_{\text{max}}$, since the transfer material which is pressed into the base material must be harder than the substrate material. This fact introduces an additional constraint on the stress $\tau$: $\tau_I$ at the transfer layer-substrate interface cannot exceed $\gamma_{\text{max}}$ of the bulk. With $\gamma^l_{\text{max}}$ and $\gamma^l$ fixed for a given sliding system, $\gamma_I$ will be a function of $\gamma^l_{S}$. Therefore, this new constraint determines an upper limit for $\gamma^l_{S}$ (7). $\gamma^l_{S}$ will be limited by $\gamma_I$, which in turn will be limited by $\gamma_{\text{max}}$, rather than by $\gamma^l_{\text{max}}$. 


For the calculation of the plastic work with this theory, it was assumed that $\tau_s^t$ is smaller than $\tau_{\text{max}}^t$ of the bulk. Fig. 6-8 shows a typical result of the curve of the normalized plastic work vs. log $T$, where $T$ is the thickness of transfer layer at the center. The following parameters were used: $(\tau_{\text{max}}/\tau_{\text{max}}^t) = 0.8$, $(\tau_s^t/\tau_{\text{max}}^t) = 0.79$, $S_0 = 40$ $\mu$m, $a = 0.07$ $\mu$m$^{-1}$. It is interesting that the plastic work of case 1 is lower than that of case 2 when $T$ is larger than 0.5 $\mu$m and smaller than 6 $\mu$m. Therefore, case 1 will be more energetically favored than case 2. However, when $T$ is smaller than 0.5 $\mu$m or larger than 6 $\mu$m, case 1 will be favored. Based on this calculation, a mechanism for the growth of transfer layers is suggested as shown in Fig. 6-9. At the beginning, when the amount of transfer material is very small, the flat transfer layer is favored, e.g., Fig. 6-9a. When the size increases to about 0.5 $\mu$m, the flat transfer layer is no longer stable, instead, any random fluctuation in depth at any place will result in a favored growth. (Fig. 6-9b) (The idea is similar to the nucleation and growth in phase transformations). As the size increases the curved transfer layer grows as the depth to width ratio, $T/S_0$, increases. But, the "driving force" (i.e., the energy difference in Fig. 6-8) for the curved growth decreases after it reaches a minimum. Until the $T/S_0$ ratio is larger than $1/6$, curved growth is not favored over flat growth. After that, the flat transfer layer has a lower plastic
Fig. 6-8 Calculated plastic energy associated with the flat and the curved transfer layer, as a function of transfer layer size.
Fig. 6-9 Sketch showing the growth process of the transfer layer.
energy, but the difference may be too small to convert the shape completely to a flat layer. As a result, the shape of the transfer layer would be a mixture of the shapes of case 1 and case 2.

It should be pointed out that type 1 and type 2 transfer layers mentioned above are merely two simple and typical cases. They were chosen for comparison because they are easier for mathematical manipulation. However, there are still many possibilities, other than those two. Ideally, one should not choose only two possibilities for comparison and determine whichever is stable. Instead, one should use numerical methods to set up a series of functions $t = f(y)$, assuming that the areas under all these $t$ vs. $y$ curves are the same, and substitute each into Eq. (6-18) to find out which shape of the transfer material is most energetically favored. Then one could vary the area under each $t - y$ curve (i.e., change the size of the transfer layer) to determine how the most favored shape is changed as the transfer layer grows. However, the tendency of the growth from flat shape to curved shape predicted by this calculation may shed some light on the growth mechanism of the transfer layer. This approach may be useful for explaining observations of Sasada (80); he found that the size of the transfer layer could range from a few micro-meters to about 100 um for different alloys.
This calculation is mainly based on the thermodynamic assumption that the lower energy state is favored. However, the author recognizes that the sliding process may deviate significantly from a reversible process. In an irreversible process the system tends to minimize the entropy production rate for a given reaction path. The entropy production rate here may depend on the growth rate of the transfer layer and the wear rate. If the entropy production rate is small during steady state sliding, i.e., low wear rate and low transfer layer growth rate, then the above thermodynamic assumption may still be valid to a certain extent. For example, if the sliding speed is slow, then the wear rate and the transfer layer growth rate is low. Therefore, it is expected that the above thermodynamic assumption would be more applicable for a low sliding speed system. The low sliding speed system is similar to the system in which a volume of ideal gas expands against a piston on which an external pressure is applied. If the external pressure is about equal to, but smaller than, the internal pressure, then the ideal gas can expand infinitesimally slowly and follow a reversible path. On the other hand, if the entropy production rate can not be minimized, then the thermodynamic consideration is no longer accurate. Instead, the kinetics of the transformation should be considered.
Chapter VII

7. DISCUSSION

7.1 Transfer Material and Wear

The connection between transfer layer and wear has been acknowledged (111) by several workers. Lancaster (112,73) used radioactive tracers and arrived at the conclusion from pin on disk experiments that all debris are generated from a transfer layer and there is no direct wear from the pin. Sasada (76-86) analysed SEM/WDX data and proposed a mechanism for the formation process of transfer layers. He suggested that "the particles are produced not from the parent surfaces directly when the surface breaks up, but through an accumulation process of numerous minute fragments separated from the surface".

The similarities between transfer layer and debris found in this investigation also indicate that transfer layers and debris are intimately connected. The evidence that supports this point of view may be summarized as follow:

(1) Similar amount of transferred Fe, i.e., about 0.5%, existed uniformly in both the transfer layer and the debris.
(2) Transfer layer and debris have similar microhardness values.

(3) The thickness of transfer layers (plateau) and debris flakes are about the same in the age hardened case.

(4) The microstructures of transfer layers and debris are similar; they consist of ultra-fine grains and oxides. The substrate material contains precipitates and extensive deformation twinning; these structural features are not visible in the transfer layer. This indicates that delamination has not occurred in the base material.

Evidence of subsurface cracks in the base material as predicted by Delamination Theory (51) has not been observed in any of the sections studied in this work, even near the hard cobalt particles. The deformed material around the particles flows smoothly, well defined cells are smoothly curved near the edges parallel to the sliding direction and cells are somewhat equi-axed near the edges perpendicular to the sliding direction. As shown in Fig. 7-1, the flow pattern is similar to that of a stream flowing around a rock.

Concerning the formation mechanism for transfer layers, Sasada proposed that transfer patches and layers develop by accumulation of small "transfer elements". The "transfer element" is formed by "a small fragment of either surface portion being sheared off and adhered onto the mating surface".
Fig. 7-1 TEM picture of longitudinal section from a solution annealed specimen after sliding. Deformed material flows smoothly around the "Co" particle.
Lancaster (112,73) and Heilmann et al (111) suggested that the original transfer particles may be smaller than the observed debris particles. Although the origin of the transfer material is still unsettled, the author would like to emphasize the important role that the "ring coating" plays during the formation of transfer layers. The ring coating should have a certain optimum thickness; when it is thick, part of the coating transfers back onto the surface as patches or it is scraped off as loose particles. When it is thin, the ring is ready to pick up new coating materials. Transfer occurs during the pick-up process, as illustrated in Fig. (7-2). During the pick-up process softer material is sheared off and flows along the harder material surface. As a result, transferred Fe is picked up by the flowing material on the ring surface and blended into the stream. The process is very similar to the flowing water of a river near the bank. The flowing water picks up material near the bank and mixes it with itself. In the case of Cu sliding against Fe, Cu and Fe correspond with the clean water and sediment, respectively, and the transfer layer corresponds to the water-sediment mixture. The transfer layer grows as this process continues, until it reaches a critical thickness; then pieces of the transfer layer are removed by frictional motion to form debris flakes.

Now the question remaining is what role the transfer plays during the formation of transfer layer. Is transfer
Fig. 7-2 Schematic diagram illustrating the growth of ring coating and transfer pick-up.
necessary in order to generate ultra-fine grained transfer material? Sasada (110) proposed that the ease of formation of transfer layers depends upon the relative solubility of the mating materials. He suggested that the maximum transfer layer thickness increases as the mutual solubility increases. This is similar to the compatibility rule of Rabinowicz (121). However, the transferred Fe was found to be α-Fe in the current studies. Earlier work by Heilmann (113) has also shown that Fe was in the form of bcc crystals instead of being elemental atoms dissolved in the copper. These observations may imply that the mutual solubility is not as important for the growth of transfer layers as Sasada expected. For example, the transfer layer in the solution annealed case can grow as thick as 20 μm, even though the mutual solubility of Cu and Fe is poor. In the author's opinion, the maximum thickness that a transfer layer can grow will depend more on the mechanical properties and the relative hardness of the sliding pair and the transfer material than merely on mutual solubilities. If the transfer layer is softer than the base, its maximum thickness will largely depend on the strain decay constant (see section 6.1). If, on the other hand, the transfer layer is harder, the size of the transfer layer will be determined by the plastic flow characteristics of the transfer material. Because the transfer layer is pressed in, plastic flow may be required for its removal.
It should be pointed out that the amount of transferred Fe in the current studies is only about 0.5 wt%. It appears to be too little to offer a significant effect on the ultra-fine grained nature of the transfer material. Recently Benjamin et al (99,100,101) published some interesting papers on mechanical alloying. Some of their results are summarized as follows:

(1) They reported that flow features were found from mechanically alloyed powders, and the spacings between flow lines decrease with increasing processing time.

(2) Equi-axed fine grains were observed by TEM. The grain size is about 0.2 μm.

(3) Small oxide particles are generated by repeatedly breaking the surface oxide film during the mechanical alloy process.

(4) The complete process involves more than simply mixing of particles on a fine scale. For example, in the Al-Mg system, Mg is dissolved even though its content is larger than the solubility limit.

Therefore, it seems that the formation of transfer layer material is in some ways similar to the early stages of the mechanical alloying process. In both cases the resulting structures and oxides are similar.

No precipitates were found in the transfer material; however BeO is evident from the TEM diffraction patterns.
It is possible that some Be has dissolved in the Cu matrix or segregated to the grain boundaries. If Be is dissolved in the Cu matrix, then the lattice parameter of copper would be decreased according to Vegard's law (122) since the Be atom is smaller than the Cu atom, i.e., 1.12Å and 1.28Å, respectively. By carefully calibrating the TEM camera constant and calculating the lattice parameter from the copper diffraction rings, the lattice parameter of Cu in debris structure was found to be smaller than that of pure copper. The lattice parameter of debris Cu is 3.499Å, while pure Cu is 3.615Å. This reduction could be caused by the relatively small diameter of the solute.

There are no available theories or experiments to describe the mechanical properties of transfer material. At this time one can only speculate about them. The possible mechanism for this material to accommodate strain may be (1) grain boundary sliding, or (2) deformation twinning. Since the grains are so small, ordinary dislocation mode deformation may not operate due to image forces. However, dislocations generated at one side of a crystal might pass completely across the crystal to the opposite side. McGinn (114) reported that twins are more likely to occur when the particle size is small. If grain boundary sliding predominates, then the ultra-fine grains may allow superplastic behavior with negligible work hardening. Plastic deformation here simply means flowing of those small particles.
As mentioned in the preceding section, the debris particles are closely connected with the transfer layer. Generally there are two kinds of debris collected: (1) large flakes (2) small powder. It is now worthwhile to describe how these two kinds of debris could arise.

It has been pointed out that the transfer layer in the case of age-hardened Cu-Be is elevated about 15 μm above the base as a surface plateau, and that the critical condition of \( D_1 > D_2 \) determines the removal of plateau material as a loose debris flake. When the plateau thickness grows to a critical value such that \( D_1 > D_2 \) is satisfied, the plateau is ready to be carried out by the rotating ring because sliding on interface 2 is now favored. Such an event causes the generation of loose flakes by two ways: (1) loosely bonded (adhered) pieces could come around on the ring and be knocked loose when they hit the entrance lip of the block scar. This would give debris at that side only; (2) very loosely "bonded" (essentially mechanically interlocked during sliding) pieces would fall off as soon as they exit from the interface region. This would give debris at the exit side. The mechanism is shown schematically in Fig. 7-3.

Both mechanisms could operate together, giving debris at both sides. Also some pieces would pass through the interface region again, perhaps repeatedly. The proposed
Fig. 7-3 Schematic diagram showing the generation of loose flakes.

Fig. 7-4 Low magnification picture showing the distribution of flakes and powders, wear test used 30 lbs. (13.6 kg) load for 3 hrs., of overaged specimen (280°C, 24 hrs.).
mechanism can explain the following two facts found during wear tests: (1) shiny flakes are generally found near the entrance and exit sides of the debris collector, while small powdered debris are distributed in two parallel lines on the collector; (2) shiny copper spots occasionally show up on the ring surface because some flakes pass through the interface region again.

Usually small powdered debris are distributed in two parallel lines on the collector, with the spacing and length equal to ring dimensions (see Fig. 7-4). This phenomenon can be related to the flake removal process. As the flake is moving toward the exit, it will remove all the powders on its way out toward its edges, just like a plow moves through sand or snow. Continuous sweeping causes the powder to migrate toward the edges of the block and eventually results in the two-lines of powdered debris on the collector. Of course, the plow need not be the moving flake, any surface roughness of the ring could also cause such an effect.

During early stages of the wear test, the growth rate of plateaus may be slow, partly because there is still small number of "transfer elements" to supply the source material for plateau growth, and partly because the plateau is just not thick enough to effectively trap and keep small particles. As shown in Fig. 7-5, once the plateau is thick, small particles are more likely to be trapped around
Fig. 7-5 Schematic diagram of the formation process of new plateau material at steady state.
the plateau edges. When small particles pile up high enough to touch the ring, shearing of these particles starts from the upper portion of the particle collection. When this occurs, sliding on interface 1 is no longer stable. As a result, sliding begins on interface 2 and this causes the generation of loose flakes. This mechanism also explains why most of the plateaus are weak and somewhat loose near the interface.

It has been mentioned in Section 6.1 that the predicted flake thickness would be affected by the thickness of ring coatings. In fact, the calculation can be generalized by assuming that (coating thickness) = B x (plateau thickness), where the B factor can be less than or greater than 1. (note that B is assumed to be 1 in Section 6.1). Now \( \mu_1 \), \( \mu_2 \) expressions can be rewritten as

\[
\mu_1 = \left(1-f(T)\right) \frac{(NA)^L}{L} \left\{ \tau_{\text{max}}^L \left[ 2-\exp(-a^L_T)-\exp(-a^L_BT) \right] \right. \\
+ \tau_{\text{max}} \exp(-a^L_T) F(T_{\text{I}}/\tau_{\text{max}}) \right. \\
+ f(T) \frac{NA}{L} \tau_{\text{max}}^L F(T_{\text{I}}/\tau_{\text{max}}) \right\} 7-1
\]

\[
\mu_2 = \left(1-f(T)\right) \frac{(NA)^L}{L} \left\{ \tau_{\text{max}}^L \left[ 1-\exp(-a^L_T-a^L_BT) \right] + \tau_{\text{max}} F(T_{\text{I}}/\tau_{\text{max}}) \right. \\
+ f(T) \frac{NA}{L} \tau_{\text{max}}^L F(T_{\text{I}}/\tau_{\text{max}}) \right\} 7-2
\]

Based on the assumption that \( \mu_1 > \mu_2 \) for the critical condition, the predicted flake thickness vs. "\( a \)" (decay constant) plot for various B factors can be obtained by using a computer (see Appendix H for program). Fig. 7-6 shows an
thin plateau grows in thickness

strain difference between the two surface increases

plateau starts to collapse

plateau grows in area

Fig. 7-6 Schematic diagram illustrating the "smearing" effect.
example with the parameters \((\frac{\tau_{max}}{\tau_{max}}) = 1.57\), \((\frac{\tau_{i}}{\tau_{max}}) = 0.6\), \((\frac{\tau_{i}}{\tau_{max}}) = 0.999\). Fig. 7-6 predicts that the debris thickness increases as ring coating thickness decreases. When the ring is not coated debris thickness is predicted to be infinite, if the ring surface is smooth and flat. However, it is impossible for plateaus to grow indefinitely. There must be some limitations for plateau growth. An example is suggested in Fig. 7-7. During the growth of the plateau, the difference between the displacements at the surface and at the bottom of the plateau increases due to the exponential decay constant. When the difference in displacements is larger than some critical value such that the leading part of the plateau can not support the load, and it collapses. Therefore, instead of growing in thickness, the plateau actually grows in length (i.e., in larger surface area). Therefore, the growth of the plateau is limited by two factors: (1) a critical thickness, \(Tc\), for delamination and (2) a critical strain difference, \((\frac{\gamma_{s} - \gamma_{I}}{\gamma_{s}})C\) for plateau area growth, where \(\gamma_{s}\) is the surface strain and \(\gamma_{I}\) is the strain at the interface. Since

\[
\gamma_{I} = \gamma_{s} \exp(-a \frac{L}{t})
\]

as a result, the critical strain difference, normalized by ( ), is

\[
\frac{\gamma_{s} - \gamma_{I}}{\gamma_{s}} = 1 - \exp(-a \frac{L}{t})
\]
Fig. 7-7 Predicted flake thickness plotted against the decay constant "a", with different thickness factors B.
Eq. (7-3) can be plotted in Fig. 7-8. According to Fig. 7-6, the critical plateau thickness for delamination increases when the ring coating thickness decreases for a given decay constant "a". For example, Tc2 is larger than Tc1 because Tc2 is associated with a thinner ring coating. Fig. 7-8 provides a criterion to determine whether a plateau will delaminate or grow in area. If \( \frac{\gamma_s - \gamma_t}{\gamma_s} \) for Tc is less than \( \left( \frac{\gamma_s - \gamma_t}{\gamma_s} \right)_c \), then the plateau delaminates; if the reverse is true, then the plateau area grows. The cases are illustrated in Fig. 7-8 by Tc1 and Tc2 respectively. The critical strain difference, \( \left( \frac{\gamma_s - \gamma_t}{\gamma_s} \right)_c \), should be related to the plastic behavior of the transfer material and the load. Since no experimental data are available for \( \left( \frac{\gamma_s - \gamma_t}{\gamma_s} \right)_c \), \( \frac{\gamma_s - \gamma_t}{\gamma_s} \) is tentatively chosen to be 0.7 for the quantitative demonstration in Fig. 7-8. Usually the ring coating thickness is not uniform and it varies during the test. Therefore, whenever the ring coating is thicker, the plateau in that part of the ring is more likely to delaminate. However, the area of the plateau tends to grow when a thin coated ring surface slides on it. Furthermore, by smearing the plateau, the ring could pick up transfer material to increase its coating thickness, which allows new transfer to occur. The growth of plateaus should be considered to grow in both thickness and area. The "smearing" described above provides the mechanism to explain how the plateau grows in area.
It is mentioned in Section 5.1 that deformation twinning dominates in age hardened wear specimens. Gadalla (38) and Thomas (41) associated twinning with low stacking fault energy. However, other than stacking fault energy, high...
strain rate and precipitates may also play important roles in twinning. Murr(124) pointed out that deformation twins are more likely to take place when the strain rate is high. The results of shock pulse loading tests (125) also support this argument.

7.3 On Solution Annealed Specimen

The structure, chemistry and hardness of the transfer layer in this case are similar to that in the age hardened case. But the geometries of the transfer layers are much different for the two cases. Because the solution annealed Cu-Be is softer than the transfer layer, the transfer layer is pressed into the base. Similar observations have been reported in other sliding systems, for example in Cu against steel (109), dispersion-hardened Cu against steel (92), 304 against 440C steel (93) and Al against steel (115) systems.

Normally the hardness of the transfer layer will be affected by factors such as:

1. degree of looseness.
2. degree of processing, or "mechanical alloying".
3. environment effects such as moisture and oxygen.
4. alloy chemistry.

The hardness of the base can be influenced by strain hardening, precipitation hardening, or dynamic recovery. Since the relative hardness of transfer layer and base material determines how the transfer layer is pressed in, and since the
relative hardness can be varied, the geometry of the transfer layer is not very regular, especially after long testing time. During the early stage of the wear test, extensive transfer material builds up near the entrance side. This built-up material is believed to be generated from the ring coating when the ring surface is entering the lip at the wear track entrance. The transfer layer thus formed is solid and well compacted. It forms first near the entrance side of the wear track. After a longer testing time, the transfer layer tends to travel across the wear surface. Some small degree of surface roughness and irregularities in the transfer layer are expected. This phenomenon is believed to be due to variations of the relative hardness, because the transfer material may not be evenly pressed due to the surface roughness.

However, compared with the age-hardened wear specimens, the wear surface in the solution-annealed case is still much smoother. No obvious surface plateau was found, and the transfer layer is generally pressed into the base material. As a result, the friction trace is less noisy and the wear particle morphology is different; i.e., it consists of fine powder, flakes and layered particles. The flakes are generated within the true wear scar, while the layered particles seem to come from the entrance or exit side of the scar.
Both dislocation structure and deformation twins were found by TEM observations. However, deformation twins seem to appear only in a certain range of distance below the wear surface. As shown in Fig. 7-9, deformation twins could only be found from about 3 μm to about 20 μm below the wear surface. Dislocation cell structures are not observed. These findings are consistent with reports on Cu-Zn (43), Cu-Ag (42), and Cu-Sn (36) alloys, and with the report of Buff (96).

The debris collected in this case were flakes with thickness of about 5 μm. Their shapes are not consistent with the observed curved nature of the transfer layer. Also, the flake thickness is much thinner than expected if the flake is generated directly from the curved transfer layer. (unless fracture occurs within the transfer layer). These findings may be explained by assuming that the flake is generated at the tip of the transfer layer when the transfer material is swept from the entrance side into the interface region. The transfer layer thickness will naturally become thinner and thinner as it flows deeper into the interface. When some critical thickness is reached, then loose debris particles are generated from the thin transfer layer by a delamination process at or near the interface between transfer material and the base material. Possibly the critical thickness could also be related to the fact that a thin hard coating yields a maximum frictional force (7,17).
Fig. 7-9 Transverse section TEM image of a solution annealed wear specimen. Note twins are well-defined in a certain region below the wear surface.
Based on the earlier assumption (Section 7.1) of $\mu_1 > \mu_2$ for delamination, one could calculate the thickness for the critical condition of $\mu_1 > \mu_2$. When the transfer layer thickness decreases $\mu_1$ increases due to the hard coating on the soft base, and, $\mu_2$ decreases since sliding on interface 2 is analogous to the sliding of the "soft (transfer layer) coated on hard (ring)" system. The soft-on-hard system yields a minimum friction at a coating thickness of about 1 $\mu$m (17). Therefore, when the thickness of the transfer layer decreases, $\mu_1$ increases but $\mu_2$ decreases. The net effect may result in $\mu_1 > \mu_2$ for delamination.

7.4 On Friction and Wear Data

In this investigation, it is found that friction and wear are very closely related to the specimen hardness. The fully age-hardened specimens have the lowest friction coefficients, and the friction coefficient increases when the specimen hardness decreases due to either overaging or underaging. The wear rate (in terms of loose debris weight/hour) seems to behave in the opposite way. The debris weight/hour for full annealed specimens is lowest, while the fully age-hardened specimen wears most severely. It is true that measuring debris weight involves certain scatter. Some of the debris are trapped near the entrance side, and some of them spread around the shaft of the wear machine. They can not be collected and accounted for in the total debris
weight. However, the tendency of loose debris weight increases with age hardening is still evident.

7.4.1 Effect of Age Hardening on Friction

The result of friction coefficient decreases with age hardening agrees with the reports of Jellision (59), Suh (69), and Wilman (67) and Tegart (58). In their reports, they seemed to attribute such an effect only to the bulk hardness. The effects of transfer layer, coated transfer material on ring, and shear strength are neglected. But, a satisfactory explanation should also take these contributions into consideration.

If metallic frictional forces arise from the contributions of shear strength and hardness, then, as predicted by adhesion theory and by the energy-based friction model, the friction coefficient is equal to the ratio of the shear strength and hardness of the sliding metals. Because of the presence of the transfer layer on the block and the transfer material coated on the ring surface, the shear stress terms in both the adhesion theory and the energy-based model should be determined by the transfer material. In the age-hardened case, the transfer material is softer than the base and it doesn't seem to be affected by over- or under aging. Therefore, the shear stress terms for different heat treated specimens should be about the same. That is to say, either the stress of shear junctions (adhesion theory) or
the surface stress (energy-based model) is essentially equal to the maximum flow stress of the transfer material. The specimen cannot be deformed by a stress greater than the maximum flow stress of the soft transfer material, if the "soft" transfer material exists at the interface of sliding.

Based on the above argument, the bulk hardness seems to play a more important role on friction coefficient than the shear strength does. It determines the geometry of the transfer layer and the total contacting area. If the bulk material is soft, e.g., the case of the solution annealed specimen, the transfer layer will be pressed in, resulting in a smooth surface. Furthermore, the contacting area at the coated ring/uncoated base interface will be larger if the base is softer. Both these two effects give a larger friction coefficient due to the larger subsurface deformed volume. For the age hardened specimens, the transfer layer cannot be pressed in; therefore, the wear surface is rough. Additionally, the contacting area per unit of load, NA/L, on the coated ring/base interface is smaller for a harder base. Combining these two effects, it is possible to explain the minimum friction for fully hardened specimens and the friction increases when the specimen is overaged.

It should be pointed out that other than the contacting area considerations mentioned above, the amount of transfer material on the specimen surface, on the ring surface, and
built up near the entrance side all contribute to the friction coefficient. Because these effects are very difficult to characterize, explanations of the friction coefficient by means of these factors can not be offered in this dissertation.

7.4.2 Effect of Age Hardening on Wear

The effect of hardness on wear basically originates from the relative hardness of the transfer layer and the base material. As mentioned earlier, the geometry of the transfer layer is significantly affected by the relative hardness (1). Since the debris and the transfer layer are closely connected, it is expected that the wear would be dependent upon the specimen hardness which determines the geometry of the transfer layer.

The wear data, in terms of debris weight per hour, presented in section (4.2) showed that age-hardened specimens wore faster than solution-annealed specimens. It is also found that both the amount of fine powder and flake debris collected from the test of solution-annealed specimens are much less than those from age hardened specimens. Therefore, the explanation of how the specimen hardness affects wear may be divided into two parts: (1) the amount of flake debris, (2) the amount of powder debris.
The generation of loose flakes involves the formation and the removal of the transfer layer. In the age-hardened case, the formation process proposed in section (7.2) indicated that the formation of a surface plateau included the piling-up of small particles and the compaction of the particle collection. If the source of small particles is sufficient, (as shown in Fig. 7-10, the wear surface generally contains a large amount of small particles), then the rate of generating loose flakes is determined by the compaction process, because once the plateau is compacted the removal of the plateau is as fast as the motion of the ring.

Now consider the generation of loose flakes in the solution-annealed case. Usually in this case the source of the transfer layer is mainly from the built-up material near the entrance side. The procedure to produce debris flakes described in section (7.3) suggests that the generation of loose flakes involves large amount of plastic flow. The transfer material should flow plastically into the wear track until it is thin enough to be removed.Comparing this "flow" process to the "pressing" step described in the agehardened case, it is apparent that the generation of loose flakes from the solution-annealed specimens should be slower than from the age-hardened specimens. Additionally, the removal of the transfer layer in the solution annealed case is expected to be slower because it may involve plowing as the "hard" transfer layer travels across the "soft" base. Also,
Fig. 7-10 SEM image of the wear surface of age hardened specimen (280°C, 6 hrs.). Small particles spread over the wear surface.
some flakes might be trapped in the wear track before they move out. The difficulty associated with the removal process again suppresses the amount of loose flakes collected.

Regarding the amount of fine powder debris, the relative hardness and the wear surface morphology may be cited to explain the difference between the solution-annealed and the age-hardened cases. Since the wear surface is rough and the base material is hard for the age-hardened specimens, many small particles may have space to stay on the surface without being pressed in. Some of these are reprocessed to produce plateaus and others are removed. In contrast, because the surface is smooth and the base is soft for the solution-annealed case, it is difficult for small particles to stay on the wear surface and to move out of the interface. Usually only a small quantity of small particles is generated from the surface; most of the transfer layer is believed to originate from the ring coating. They are generated either by transferring directly from the ring coating back onto the wear surface or by scrubbing off the ring coating near the entrance side. Due to the scarcity of small particles and the difficulties in removing them, the amount of powdered debris is expected to be less in the solution annealed case.

It seems that a transition of the wear behavior occurs at a specimen hardness of about KHN 300. Such a transition
depends on the relative hardness of the transfer layer and the base material. Therefore, if the relative hardness can be artificially controlled, then it seems possible to improve the wear performance of a material. In general, the bulk hardness should be high for load capacity considerations. Therefore, the transfer material must be harder than the highly deformed base to prevent high wear rates. Possible ways to increase transfer layer hardness could be by grain boundary strengthening, oxide dispersion hardening... etc.. Grain boundary strengthening can inhibit grain boundary sliding; i.e., the flow of ultra-fine grains would be inhibited. Seah (117) suggested that the addition of Pb,Mo may strengthen the grain boundaries. Oxide dispersions may be achieved by plasma deposition (60,119) or by adding readily oxidized solutes. But, excessive amounts of some oxides may suppress the compatibility between the particles. This may increase the looseness of the transfer layer, and hence, reduce the hardness.
Chapter VIII
8. SUMMARY

1. Aged Cu-Be samples twin extensively during sliding. At least four twin systems were found in the grains below the transfer layer. In solution-annealed Cu-Be specimens, both deformation twins and dislocations appeared, but dislocations dominate in high strain and low strain regions.

2. Transfer material exists in the interface region of the sliding pair. Part of it is coated on the ring surface, and part of it spreads over the block surface. The transfer material has a microcomposite nature; i.e., it contains ultra-fine grains, oxides and transferred Fe from the ring. Optical examination shows that flow features of the transfer material are similar to those which appear in mechanically alloyed powders.

3. Transfer material contains the following four phases: (a). fcc copper (50 -- 300Å) with microtwins in the grains, (b). Cu$_2$O (about 50Å), (c). BeO (about 50Å), (d). Crystalline α-Fe.

4. Features found in the base material (precipitates, extensive twinning, etc.) are not found in the debris structure. Also, no evidence of cracks in the base material was
observed, even near the relatively large "Co" particles. These facts indicate that wear particles are not produced by delaminating the base material.

5. The microstructures of the debris (flakes and powders), transfer layer and the coated material on the ring surface are similar to each other. Wear debris are closely connected to both the transfer layer on the substrate surface and coated material on the ring.

6. Relative hardness between the base and the transfer layer largely affect the wear surface roughness and the transfer layer geometry. In the age-hardened Cu-Be specimens, the wear surface is rough and the transfer layer occurs as elevated plateaus because the transfer layer is softer than the base material. On the other hand, in solution-annealed Cu-Be specimens, the wear surface is smooth and the transfer layer is pressed in to form a parallel array of cylindrical sections.

7. A fully age-hardened specimen has a minimum friction coefficient. The friction coefficient increases either when the specimen is overaged or when it is solution-annealed. That is, the friction coefficient decreases as the specimen hardness increases. A transition from high friction to low friction seems to occur at the specimen hardness of about 300KHN.
8. A fully age-hardened specimen wears faster than solution-annealed Cu-Be alloy. Wear performance is closely related to the surface roughness and the transfer layer geometry, and these are significantly affected by the relative hardness between the transfer layer and the base material.

9. Friction coefficients at different "active" sliding interfaces, e.g., interface 1 and interface 2 in section 6.1, provide the criterion for delamination. The critical condition of $\mu_1 > \mu_2$ determines the generation of loose flakes. The growth of plateau thickness is limited by "smearing" and delamination effects. Smearing results in the growth of plateau area, while delamination based on $\mu_1 > \mu_2$ causes loose flakes.

10. The transfer material hardness is not affected by heat treatment of test samples. In fact, hardness of the transfer material is similar to the hardness of the transfer material generated during tests with OFHC Cu and dispersion hardened copper.
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115. W. A. Glaeser, private communication, Columbus Battelle Lab., 1982.


APPENDIX A

Calculation of the plateau thickness from taper-sectioned specimens.

The geometry of the taper section used in the research is shown in Fig. A-1.

\[ R = \text{radius of the ring}=17.5\text{mm} \]
\[ T = \text{thickness of plateau} \]
\[ \theta = \text{taper angle} \]
\[ w = \text{measured plateau length along sliding direction from the taper section.} \]
\[ d = \text{width of the plated Cu that remains after mechanical polishing} \]

It is clear from Fig. A-1 that
\[ \theta = \sin^{-1}(d/2R) \]

Therefore, \[ T = w \sin \sin^{-1}(d/2R) \] because \( R \gg w \) and \( \theta \) is very small (about 4°).
APPENDIX B

The Calculation of Electron Diffraction Pattern containing twin

Methods for calculating twin spots of electron diffraction pattern have been extensive studied (125, 127). A general method for the calculation proposed by O. Johari and G. Thomas was used in the current investigation.

The general expression for the transformation of twinning is

\[
\begin{pmatrix}
\frac{-h^2+k^2+l^2}{h^2+k^2+l^2} & \frac{-2hk}{h^2+k^2+l^2} & \frac{-2hl}{h^2+k^2+l^2} \\
\frac{-2hk}{h^2+k^2+l^2} & \frac{-k^2+h^2+l^2}{h^2+k^2+l^2} & \frac{-2kl}{h^2+k^2+l^2} \\
\frac{-2hl}{h^2+k^2+l^2} & \frac{-2kl}{h^2+k^2+l^2} & \frac{-l^2+k^2+h^2}{h^2+k^2+l^2}
\end{pmatrix}
\]

where \( h, k, l \) are the indices of twin plane. This matrix is much simplified for the (111) twinning plane usually found in fcc crystals. For example, if the twin plane is (1\( \overline{1} \)1), the matrix is then

\[
\begin{pmatrix}
1/3 \\
1/3
\end{pmatrix}
\begin{pmatrix}
1 & 2 & -2 \\
2 & 1 & 2 \\
-2 & 2 & 1
\end{pmatrix}
\]

Now one can calculate the twin spots associated with an (011) diffraction pattern. Since (011) is an invariant vector after twinning, i.e.,
therefore, the \((011)_{\text{tw}}\) and \((011)_{\text{mat}}\) diffraction pattern will be superimposed with each other. After transformation the parent matrix spots become

\[
\begin{align*}
1\overline{1}1 & \rightarrow \overline{1}1\overline{1} \\
\overline{1}1\overline{1} & \rightarrow 1\overline{1}1 \\
\overline{1}1\overline{1} & \rightarrow 1/3(\overline{5}1\overline{1}) \\
1\overline{1}\overline{1} & \rightarrow 1/3(51\overline{1}) \\
200 & \rightarrow 1/3(24\overline{4}) \\
\overline{2}00 & \rightarrow 1/3(\overline{2}4\overline{4})
\end{align*}
\]

Therefore the twin spots can be positioned as follow:

\[\text{\begin{tikzpicture}
\draw[blue] (0,0) node [draw,fill] (a) {};
\draw[blue] (0,1) node [draw,fill] (b) {};
\draw[blue] (0,2) node [draw,fill] (c) {};
\draw[blue] (0,-1) node [draw,fill] (d) {};
\end{tikzpicture}}\]

\text{\begin{tikzpicture}
\draw[blue] (0,0) node [draw,fill] (a) {};
\draw[blue] (0,1) node [draw,fill] (b) {};
\draw[blue] (0,2) node [draw,fill] (c) {};
\draw[blue] (0,-1) node [draw,fill] (d) {};
\end{tikzpicture}}\]

\[\text{\begin{tikzpicture}
\draw[blue] (0,0) node [draw,fill] (a) {};
\draw[blue] (0,1) node [draw,fill] (b) {};
\draw[blue] (0,2) node [draw,fill] (c) {};
\draw[blue] (0,-1) node [draw,fill] (d) {};
\end{tikzpicture}}\]

\[\text{\begin{tikzpicture}
\draw[blue] (0,0) node [draw,fill] (a) {};
\draw[blue] (0,1) node [draw,fill] (b) {};
\draw[blue] (0,2) node [draw,fill] (c) {};
\draw[blue] (0,-1) node [draw,fill] (d) {};
\end{tikzpicture}}\]

\[\text{\begin{tikzpicture}
\draw[blue] (0,0) node [draw,fill] (a) {};
\draw[blue] (0,1) node [draw,fill] (b) {};
\draw[blue] (0,2) node [draw,fill] (c) {};
\draw[blue] (0,-1) node [draw,fill] (d) {};
\end{tikzpicture}}\]

\[\text{\begin{tikzpicture}
\draw[blue] (0,0) node [draw,fill] (a) {};
\draw[blue] (0,1) node [draw,fill] (b) {};
\draw[blue] (0,2) node [draw,fill] (c) {};
\draw[blue] (0,-1) node [draw,fill] (d) {};
\end{tikzpicture}}\]

\[\text{\begin{tikzpicture}
\draw[blue] (0,0) node [draw,fill] (a) {};
\draw[blue] (0,1) node [draw,fill] (b) {};
\draw[blue] (0,2) node [draw,fill] (c) {};
\draw[blue] (0,-1) node [draw,fill] (d) {};
\end{tikzpicture}}\]

\[\text{\begin{tikzpicture}
\draw[blue] (0,0) node [draw,fill] (a) {};
\draw[blue] (0,1) node [draw,fill] (b) {};
\draw[blue] (0,2) node [draw,fill] (c) {};
\draw[blue] (0,-1) node [draw,fill] (d) {};
\end{tikzpicture}}\]

\[\text{\begin{tikzpicture}
\draw[blue] (0,0) node [draw,fill] (a) {};
\draw[blue] (0,1) node [draw,fill] (b) {};
\draw[blue] (0,2) node [draw,fill] (c) {};
\draw[blue] (0,-1) node [draw,fill] (d) {};
\end{tikzpicture}}\]

\[\text{\begin{tikzpicture}
\draw[blue] (0,0) node [draw,fill] (a) {};
\draw[blue] (0,1) node [draw,fill] (b) {};
\draw[blue] (0,2) node [draw,fill] (c) {};
\draw[blue] (0,-1) node [draw,fill] (d) {};
\end{tikzpicture}}\]

Each of those twin spots essentially is rotated about \((011)\), the beam axis, by 70.5°.

Similarly, if the twin plane is \((\overline{1}1\overline{1})\), then the twin spots' positions after transformation will be

\[
\begin{align*}
1\overline{1}\overline{1} & \rightarrow \overline{1}\overline{1}\overline{1} \\
\overline{1}\overline{1}\overline{1} & \rightarrow 1\overline{1}\overline{1} \\
\overline{1}\overline{1}\overline{1} & \rightarrow 1/3(5\overline{1}\overline{1}) \\
1\overline{1}\overline{1} & \rightarrow 1/3(5\overline{1}\overline{1})
\end{align*}
\]
resulting in the following pattern

combining the above two sets of twin spots, i.e., diffracting twin1, twin2 and the parent matrix at the same time, one is able to obtain the complete diffraction pattern as

This diffraction pattern is exactly the same as in Fig.5-28 in section 5.2.
### APPENDIX C

#### Lattice Parameters and d-spacings of the Phases of Interest

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<td>(111) (111) (111) (200) (112)</td>
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<td></td>
<td>1.866</td>
<td>(222)</td>
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<td>2.027</td>
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<td>1.161</td>
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<td></td>
<td>2.70</td>
<td>(101) (120) (121) (130) (031)</td>
</tr>
<tr>
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<td>3.35</td>
<td>(110) (101) (120) (121) (130) (031)</td>
</tr>
<tr>
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<td>1.316</td>
<td>(012) (022) (122)</td>
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APPENDIX D

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DIMENSION BUF(20)
DIMENSION FL1(201), FL2(201), FS(201)

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TYPE 110
FORMAT('/', ' XM=(NA)/L/(NA)LF= ?')
READ(5, *) XM

TYPE 130
FORMAT('/', ' U=TAU/TAUMAX = ?')
READ(5, *) U

TYPE 135
FORMAT('/', ' V=TAUS/TAUMAX = ?')
READ(5, *) V

TYPE 140
FORMAT('/', ' W=TAUMAX/TAUMAXL= ?')
READ(5, *) W

TYPE 145
FORMAT('/', ' A=RELAXATION FACTOR= ?')
READ(5, *) A

TYPE 150
FORMAT('/', ' C=COATING THICKNESS= ?')
READ(5, *) C

T(I)=0.0000
DO 500 I=1, 201
XT=T(I)
CALL MHT(XT; U, V, F1, F2, F3)
FL1(I)=F1
FL2(I)=F2
FS(I)=F3
P=2.0-EXP(-(A*T(I)))-EXP(-A*C)
Q=U*EXP(-A*T(I))*FL1(I)
R=1.0-EXP(-(C+1)/A)+W*FL1(I)
S=W*FL1(I)
Y1(I)=(1.0-FS(I)) *(2.0-EXP(-(A*T(I)))*FL1(I))+EXP(-A*C)
Y2(I)=(1.0-FS(I)) *(1.0-EXP(-(T(I)+C)/A))*W*FL1(I)+FS(I)*
XM*W*FL2(I)
IF(I .EQ. 201) GOTO 500
T(I+1)=T(I)+0.25
WRITE(6, 409) XT, Y1(I), Y2(I), P, Q, R, S
500 CONTINUE
CALL PLTSET(BUF)
CALL PLTSCL(BUF, 0, 50, 0, 2.5, 2, 1, 10, 7)
CALL PLTAXS(BUF,6,1,0)
CALL PLTSMV(BUF,0,0,0)
CALL PENDN
DO 700 I=1,201
  CALL PLTSMV(BUF,T(I),Y1(I))
700  CONTINUE
CALL PENUP
CALL PLTSMV(BUF,0,0,0)
CALL PENDN
DO 710 I=1,201
  CALL PLTSMV(BUF,T(I),Y2(I))
710  CONTINUE
CALL PENUP
CALL PLTMKR(BUF,48,Y1(192),1,2)
CALL PLTMKR(BUF,48,Y2(192),2,2)
CLOSE (UNIT=10)
TYPE 160
160 FORMAT(/,' INPUT 111=STOP OTHERWISE CONTINUE '*$)
READ(5,**K)
IF(K .NE. 111)GOTO 600
STOP
END

C
C
SUBROUTINE MET(XT,U,V,F1,F2,F3)
F1=1.0-2.0*(ALOG(1.0+U)-U)/(ALOG(1.0-U)**2))
F2=1.0-2.0*(ALOG(1.0+V)-V)/(ALOG(1.0-V)**2))
F3=0.5*(TANH(2.0-4.0*XT)+1.0)
RETURN
END
APPENDIX E

FILE NAME: JARSU, FOR
BYTE CHAR(30)
DIMENSION T(300), Y1(300), Y2(300)
DIMENSION BUF(30), Z(102)
DIMENSION FS(201), R(17)

800 CONTINUE
TYPE 100
100 FORMAT(/,'1        XN=(NA)L/(NA)LP= ?'$/)
READ(5,*)XN
TYPE 110
110 FORMAT(/,'        XN=(NA)//(NA)LF = ?'$/)
READ(5,*)XH
TYPE 130
130 FORMAT(/,'        U0=TAU1/TAUMAX =?$/)
READ(5,*)U
TYPE 145
145 FORMAT(/,'        AO=RELAXATION FACTOR=?'$/)
READ(5,*)A
TYPE 150
150 FORMAT(/,'        B=THICKNESS FACTOR=?'$/)
READ(5,*)B
TYPE 159
159 FORMAT(/,'        HOW MANY CURVE DO YOU WANT TO PLOT ? '$/)
READ(5,*)PLOT
CALL PLTSET(BUF)
CALL PLTSCS(BUF,0.,1.0,0.,50.,2.1,10,7.)
CALL PLTAXS(BUF,6.,0,6)
T(1)=0.0000
Z(1)=U
R(1)=A
DO 600 K=1,10
XU=R(K)
DO 550 J=1,10G
XU=Z(J)
FL1=1.0-2.0*(ALOG(1.0+XU)-XU)/(ALOG(1.0-XU**2))
V=0.999
FL2=1.0-2.0*(ALOG(1.0+V)-V)/(ALOG(1.0-V**2))
W=1.0/XU
DO 500 I=1,201
XT=T(I)
CALL MET(XT,F3)
FS(I)=F3
Y1(I)=(1.0-FS(I))*(2.0-(EXP(-XAT(I)))*EXP(-XABT(I)))+
1+W*(EXP(-XAT(I))*FL1)*XN+FS(I)*XM*W*FL2
Y2(I)=(1.0-FS(I))*(1.0-EXP(-(1.0+B)*XAT(I)))+W*FL1+FS(I)
1*XM*W*FL2
IF(I-5)305,305,306
306 Q=Y1(I)-Y2(I)
IF(Q-ABS(Q) .EQ. 0) GO TO 308
IF(I .EQ. 201) GOTO 542
GO TO 305
305 CONTINUE
T(I+1)=T(I)+0.25
500 CONTINUE
308 IF(J .GT. 1.0) GO TO 541
CALL PLTSMV(BUF,U,T(I))
CALL PENIN
GO TO 542
541 CALL PLTSMV(BUF,Z(J),T(I)-0.125)
542 Z(J+1)=Z(J)+0.00?
IF(J .EQ. 60) GO TO 550
550 CONTINUE
CALL PENUP
R(K+1)=R(K)+0.01
IF(K .EQ. PLOT) GO TO 609
600 CONTINUE
609 CALL PLTSMV(BUF,0.075,60.)
WRITE(7,10)
10 FORMAT(/, ' NAME OF PLOT: ',$)
READ(5,20) NCHAR, CHAR
20 FORMAT(9,20A1)
CALL PLTSTR(BUF,CHAR,NCHAR,3.,1)
CALL PLTSMV(BUF,0.075,55.)
WRITE(7,70)
70 FORMAT(' VARIABLES: ',$)
READ(5,80) NCHAR, CHAR
80 FORMAT(9,80A1)
CALL PLTSTR(BUF,CHAR,NCHAR,2.,1)
CALL PLTSMV(BUF,-0.1,5.)
WRITE(7,30)
30 FORMAT(' LABELE OF Y-AXIS: ',$)
READ(5,40) NCHAR, CHAR
40 FORMAT(9,40A1)
CALL PLTSTR(BUF,CHAR,NCHAR,3.,4)
CALL PLTSMV(BUF,0.2,-8.)
WRITE(7,50)
50 FORMAT(' LABELE OF X-AXIS: ',$)
READ(5,60) NCHAR, CHAR
60 FORMAT(9,60A1)
CALL PLTSTR(BUF,CHAR,NCHAR,3.,1)
CLOSE(UNIT=10)
TYPE 160
160 FORMAT(//,' INPUT 111=STOP, OTHERWISE CONTINUE '$)
READ(5,**) K
IF(K .NE. 111) GOTO 800
STOP
END
C
C
SUBROUTINE MET(XT,F3)
F3=0.5*(TANH(2.0-4.0*XT)+1.0)
RETURN
END
FILE NAME: JARSA.FOR

BYTE CHAR(30)
DIMENSION T(300), Y1(300), Y2(300)
DIMENSION BUF(30), Z(102)
DIMENSION FL1(201), FL2(201), FS(201)

CONTINUE

TYPE 100
FORMAT('/','1 XN=(NA)L/(NA)LP= ?\$')
READ(5,*), XN

TYPE 110
FORMAT('/',' XM=(NA)/(NA)LP = ?\$')
READ(5,*), XM

TYPE 130
FORMAT('/',' U=TAUI/TAUMAX = ?\$')
READ(5,*), U

TYPE 135
FORMAT('/',' V=TAUS/TAUMAX = ?\$')
READ(5,*), V

TYPE 140
FORMAT('/',' W=TAUMAX/TAUMAX= ?\$')
READ(5,*), W

TYPE 145
FORMAT('/',' AO=RELAXATION FACTOR= ?\$')
READ(5,*), AO

TYPE 150
FORMAT('/',' B=THICKNESS FACTOR= ?\$')
READ(5,*), B

CALL FLYSET(BUF)
CALL PLTSCL(BUF, 0, 0, 0.25, 0, 50, 0, 2, 1, 10, 7)
CALL PLTAXS(BUF, 6, C, 0)

T(I) = 0.0000
Z(I) = A
DO 550 J = 1, 63
XZ = Z(J)
DO 500 I = 1, 201
XT = T(I)
CALL MET(XT, U, V, FL1, FL2, FS)

FL1(I) = F1
FL2(I) = F2
FS(I) = F3

Y1(I) = (1.0 - FS(I)) * (2.0 - (EXP(-XZ*T(I)) + EXP(-XZ*B*T(I)))).
1 + W * EXP(-XZ*T(I)) * FL1(I) * FL2(I) * FS(I)
Y2(I) = (1.0 - FS(I)) * ((1.0 - EXP(-(1.0 + B) * XZ*T(I))) + W * FL1(I) * FS(I)
1 * XM * KM * FL2(I)

IF(I-5) = 305, 305, 306
G = Y1(I) - Y2(I)

IF(Q = ABS(Q), EQ. 0) GO TO 308
IF(I .EQ. 201)GOTO 540
GO TO 305

305 CONTINUE
   T(I+1)=T(I)+0.25

500 CONTINUE

540 IF(J.GT.1.0)GO TO 541
   CALL PLTSMV(BUF,0.001,50.)
   CALL PENDN
   GO TO 542

308 CALL PENDN
   CALL PLTSMV(BUF,Z(J),T(I)-0.125)

542 Z(J+1)=Z(J)+0.004
   IF(J.EQ.63)GO TO 550

550 CONTINUE
   CALL PENUP
   CALL PLTSMV(BUF,0.075;0.)
   WRITE(7,10)

10 FORMAT('NAME OF PLOT: ',*)
   READ(5,20)NCHAR,CHAR

20 FORMAT(0,20A1)
   CALL PLTSTR(BUF,CHAR,NCHAR,3,1)
   CALL PLTSMV(BUF,0.075,55.)
   WRITE(7,70)

70 FORMAT('VARIABLES: ',*)
   READ(5,80)NCHAR,CHAR

80 FORMAT(0,80A1)
   CALL PLTSTR(BUF,CHAR,NCHAR,2,1)
   CALL PLTSMV(BUF,-0.025,5.)
   WRITE(7,30)

30 FORMAT('LABEL OF Y-AXIS: ',*)
   READ(5,40)NCHAR,CHAR

40 FORMAT(0,40A1)
   CALL PLTSTR(BUF,CHAR,NCHAR,3,4)
   CALL PLTSMV(BUF,0.125,-3.)
   WRITE(7,50)

50 FORMAT('LABEL OF X-AXIS: ',*)
   READ(5,60)NCHAR,CHAR

60 FORMAT(0,60A1)
   CALL PLTSTR(BUF,CHAR,NCHAR,3,1)
   CLOSE UNIT=10;
   TYPE 160

160 FORMAT(,10,'INPUT 111=STOP, OTHERWISE CONTINUE '*)
   READ(5,*)K
   IF(K. NE. 111)GOTO 800
   STOP
   END
SUBROUTINE MET(X,T,U,V,F1,F2,F3)
F1=1.0-2.0*(ALOG(1.0+U)-U)/(ALOG(1.0-U**2))
F2=1.0-2.0*(ALOG(1.0+V)-V)/(ALOG(1.0-V**2))
F3=0.5*(TANH(2.0-4.0*X)+1.0)
RETURN
END
APPENDIX G

C
C FILE NAME: JARSAO.FOR
BYTE CHAR(30)
DIMENSION T(300), Y1(300), Y2(300)
DIMENSION BUF(30), Z(102), R(17)
DIMENSION FL1(201), FL2(201), FS(201)
C
C
800 CONTINUE
TYPE 100
100 FORMAT(/,'1 X N = (N A) L / (N A) L P = ?' $)
READ(5,*), X N
TYPE 110
110 FORMAT(/,' X M = (N A) / (N A) L P = ?' $)
READ(5,*), X M
TYPE 120
120 FORMAT(/,' U = T A U I T A U M A X = ?' $)
READ(5,*), U
TYPE 130
130 FORMAT(/,' V = T A U S T A U M A X = ?' $)
READ(5,*), V
TYPE 140
140 FORMAT(/,' W = T A U M A X / T A U M A X L = ?' $)
READ(5,*), W
TYPE 150
150 FORMAT(/,' A 0 = R E L A X A T I O N F A C T O R = ?' $)
READ(5,*), A 0
TYPE 159
159 FORMAT(/,' HOW M A N Y C U R V E S D O Y O U W A N T T O F L O T ? ' $)
READ(5,*), P L O T
CALL PLTSET(BUF)
CALL PLTSCL(BUF, 0., 0., 0., 25, 0., 50., 2., 1., 10., 7.)
CALL PLTAXS(BUF, 6, 0, 0)
R(1) = B
T(1) = 0.0000
Z(1) = A
DO 600 K = 1, 16
XR = R(K)
DO 550 J = 1, 63
XZ = Z(J)
DO 500 I = 1, 201
XT = T(I)
CALL MET(XT, U, V, F1, F2, F3)
FL1(I) = F1
FL2(I) = F2
FS(I) = F3
Y1(I) = (1.0 - FS(I)) * (2.0 - (EXP(-XZ*T(I)) + EXP(-XZ*R(K)*T(I))))
1 + W * EXP(-XZ*T(I))*FL1(I)*XN+FS(I)*XM*W*FL2(I)
Y2(I)=(1.0-FS(I))\times(1.0-\exp(-(1.0+R(K))\times XZ*T(I)))+W*FL1(I)
I + FS(I)*XM*W*FL2(I)
IF(I-5) 305,305,306
306 Q=Y1(I)-Y2(I)
IF(Q=ABS(Q)=EQ. 0)GO TO 308
IF(I, EQ. 201)GOTO 540
GO TO 305
305 CONTINUE
T(I+1)=T(I)+0.25
500 CONTINUE
540 IF(J .GT. 1.0)GO TO 541
CALL PLTSMV(BUF,0.001,50.)
CALL PEND
GO TO 542
541 CALL PLTSMV(BUF,Z(J),50.)
GO TO 542
308 CALL PLTSMV(BUF,Z(J),T(I)-0.125)
542 Z(J+1)=Z(J)+0.004
IF(J, EQ. 63)GO TO 550
550 CONTINUE
CALL PENUP
IF(K, EQ. PLOT)GO TO 601
R(K+1)=R(K)+0.2
600 CONTINUE
601 CALL PENUP
CALL PLTSMV(BUF,0.075,60.)
WRITE(7,10)
10 FORMAT(/'NAME OF PLOT:'$)
READ(5,20)NCHAR, CHAR
20 FORMAT(0,20A1)
CALL PLTSTR(BUF,CHAR,NCHAR,3,1)
CALL PLTSMV(BUF,0.075,55.)
WRITE(7,30)
30 FORMAT(/'VARIABLES:'$)
READ(5,40)NCHAR, CHAR
40 FORMAT(0,40A1)
CALL PLTSTR(BUF,CHAR,NCHAR,2,1)
CALL PLTSMV(BUF,-0.02,5.)
WRITE(7,50)
50 FORMAT(/'LABEL OF Y-AXIS:'$)
READ(5,60)NCHAR, CHAR
60 FORMAT(0,60A1)
CALL PLTSTR(BUF,CHAR,NCHAR,3,4)
CALL PLTSMV(BUF,0.125,8.)
WRITE(7,70)
70 FORMAT(/'LABEL OF X-AXIS:'$)
READ(5,80)NCHAR, CHAR
80 FORMAT(0,80A1)
CALL PLTSTR(BUF,CHAR,NCHAR,3,1)
CLOSE (UNIT=10)
TYPE 160
160 FORMAT(/' INPUT 111=STOP, OTHERWISE CONTINUE '$/)
READ(5,*)K
IF(K .NE. 111)GO TO 800
STOP
END

SUBROUTINE MET(XT,U,V,F1,F2,F3)
F1=1.0-2.0*(ALOG(1.0+U)-U)/(ALOG(1.0-U**2))
F2=1.0-2.0*(ALOG(1.0+V)-V)/(ALOG(1.0-V**2))
F3=0.5*(TANH(2.0-4.0*XT)+1.0)
RETURN
END
FILE NAME: TRANSL.FOR
DIMENSION BUF(30)
DIMENSION Y(205), YF(205)
DIMENSION R(105), A02(205), G2(205)
DIMENSION A01(205), G1(205)
BYTE CHAR(30)

CONTINUE

TYPE 100
FORMAT(/r'1 B=GL/GB = ?'$
READ(5,*):B

TYPE 102
FORMAT(/r' U=lm/TmL = ?'$
READ(5,*):U

TYPE 103
FORMAT(/r' V=TsL/TmL = ?'$
READ(5,*):V

TYPE 107
FORMAT(/r' SO=BUMP WIDTH= ?'$)
READ(5,*):SO

TYPE 105
FORMAT(/r' A=Decay factor = ?'$)
READ(5,*):A

CALL PLOTSET(BUF)
CALL PLOTSCL(BUF,-0.5,1.5,0.9,1.3,2.1,1.5,8.5,6.)
CALL PLOTAXS(BUF,5+0,0)
R(1)=465.+0.5*SO
DO 400 J=1,31
XR=R(J)
Y(1)=0.000
AG2(0)=0.000
DO 500 I=1,200
XY=Y(I)
DO=ATAN(((SO/2.)**2.)/(ABS(XR**2.-(SO/2.))**2.))**0.5
XT=(2./SO)*0.5*00*(XR**2.)-0.25*SO*XR*COS(00)
W=1.-((1.-((V**2.)))**(EXP(-A*XT)))**0.5
Q=W/U
F2=1.-2.*(ALOG(1.+V)-V)/(ALOG(1.-V)**2.)
F3=1.-2.*(ALOG(1.+W)-W)/(ALOG(1.-W)**2.)
F4=1.-2.*(ALOG(1.+Q)-Q)/(ALOG(1.-Q)**2.)
F5=0.5*(TANH(2.-4.*XT)+1.)
G2(I)=(SO/200.)**((1.-F5)**2.)*((1.-EXP(-A*XT)**(F3/F2)+U*EXP(-A*XT)
1.*(F4/F2))+F5)*SO
AG2(I)=G2(I)+AG2(I-1)
Y(I+1)=Y(I)+0.2
IF(I.EQ. 201) GO TO 500
CONTINUE

500 CONTINUE
D = XR - ((ABS(XR**2, -(0.5*S0)**2))**0.5)

IF(J .GT. 1) GO TO 501
CALL PLTSMV(BUF, ALOG(D)/ALOG(10.), AG1(200))
CALL PENDN
GO TO 502

501 CALL PLTSMV(BUF, ALOG(D)/ALOG(10.), AG1(200))

502 IF(J .GT. 25) GO TO 390
R(J+1) = R(J) - 31. + J
GO TO 400

390 IF(J .GT. 29) GO TO 391
R(J+1) = R(J) - (R(26) - 0.5*S0 - 0.01)/7.
GO TO 400

391 R(J+1) = 0.5*S0 + 0.01

400 CONTINUE
CALL PENUP
R(1) = 465. + 0.5*S0
DO 600 L = 1, 31
XR = R(L)
YP(1) = 0.000
AG1(0) = 0.000
DO 300 K = 1, 201
XYP = YP(K)
XTF = ((XR**2, -(ABS(0.5*S0 - XYP)**2))**0.5 - (XR**2, -(0.5*S0)**2))
1 **0.5
W = (1. - (1, -(V**2,)))***(EXP(-A*XTP))**0.5
Q = W/U
F2 = 1. - 2.**(ALOG(1, +V) - V)/(ALOG(1, -V**2,))
F3 = 1. - 2.**(ALOG(1, +W) - W)/(ALOG(1, -W**2,))
F4 = 1. - 2.**(ALOG(1, +Q) - Q)/(ALOG(1, -Q**2,))
F5 = 0.5*(TANH(2, -4.**XTF) + 1.)
G1(K) = (1. - F5) * B * (1. - EXP(-A*XTP) * (F3/F2) + U*EXP(-A*XTP))
1 * (F4/F2)) + F5)/200.
AG1(K) = G1(K) + AG1(K-1)
YP(K+1) = YP(K) + S0/200.
IF(K .EQ. 201) GO TO 300

300 CONTINUE
DD = XR - ((XR**2, -(0.5*S0)**2))**0.5
IF(L .GT. 1) GO TO 301
CALL PLTSMV(BUF, ALOG(DD)/ALOG(10.), AG1(200))
CALL PENDN
GO TO 302

301 CALL PLTSMV(BUF, ALOG(DD)/ALOG(10.), AG1(200))

302 IF(L .GT. 25) GO TO 590
R(L+1) = R(L) - 31. + L
GO TO 600

590 IF(L .GT. 29) GO TO 591
R(L+1) = R(L) - (R(26) - 0.5*S0 - 0.01)/7.
GO TO 600

591 R(L+1) = 0.5*S0 + 0.01

600 CONTINUE
CALL PENUP
CLOSE (UNIT=10)
TYPE 106
106 FORMAT(/' ', TYPE 111 TO STOP, OTHERWISE CONTINUE ' $' )
READ(5,* ) K
IF(K .NE. 111) GO TO 800
STOP
END